Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 4959–4966
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis of ferrocenoate esters, amides and other ferrocenoyl derivatives using ferrocenoyl fluoride. A comparison of the reactions of ferrocenoyl fluoride in [bmim][BF_4] with the microwave-promoted solvent-free reactions of ferrocenoyl fluoride

Christopher Imrie *, Elago R.T. Elago, Nadia Williams, Cedric W. McCleland, Pieter Engelbrecht

Department of Chemistry, University of Port Elizabeth,[1] P.O. Box 1600, Port Elizabeth 6000, South Africa

Received 24 May 2005; received in revised form 8 August 2005; accepted 8 August 2005
Available online 23 September 2005

Abstract

Simple, efficient and convenient routes for the synthesis of ferrocenoyl derivatives are described. They involve either the reaction of nucleophilic compounds and DMAP with ferrocenoyl fluoride in [bmim][BF_4] or the solvent-free reactions of nucleophilic compounds with ferrocenoyl fluoride promoted by microwaves.

Keywords: Ferrocenoate esters; Ferrocenoate amides; Ionic liquids; Ferrocenoyl fluoride; Solvent-free synthesis; Microwave-promoted synthesis

1. Introduction

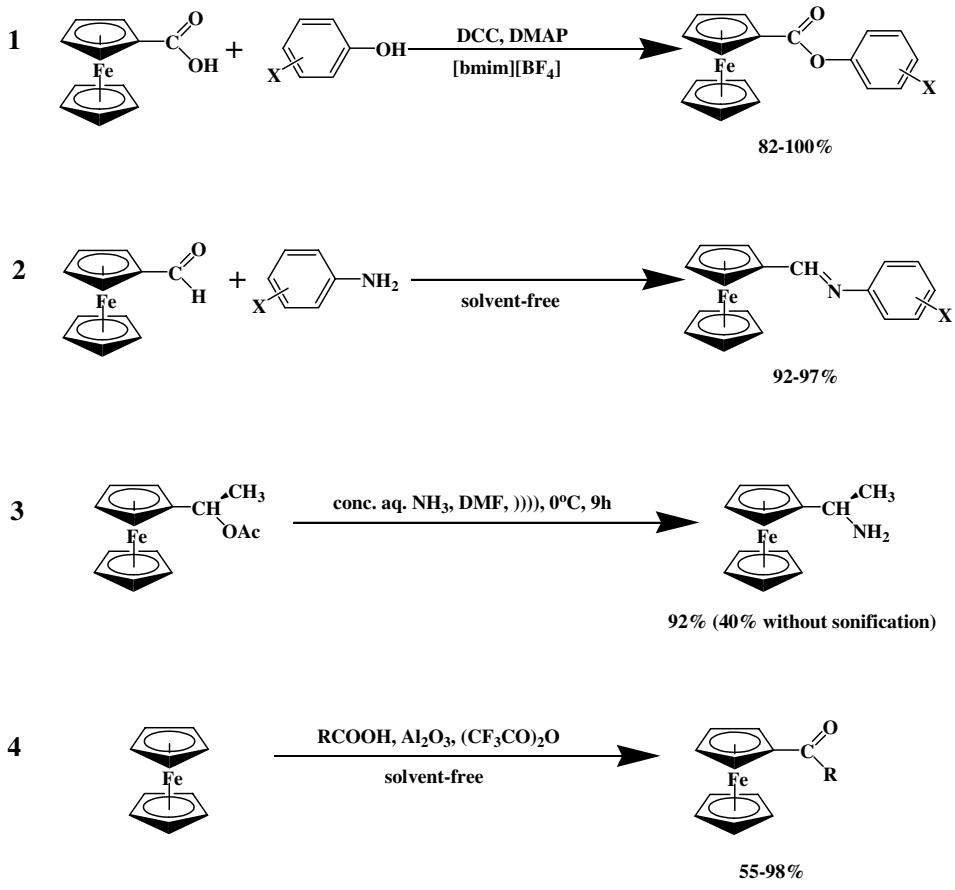
The subject of green chemistry is currently guided by a series of 12 principles [1]. Organometallic chemistry can be considered from two perspectives in relation to green chemistry. Firstly, organometallic complexes and compounds can take an active role in achieving a green chemistry principle. For example, one of the principles states that "it is better to use catalytic processes than the stoichiometric variety." Alternatively, the green chemistry principles can be applied in the synthesis of organometallic complexes. Several contributions have been made for example in relation to green chemistry and ferrocene derivatives. In many cases, ferrocene derivatives have been synthesized in alternative reaction media to volatile organic solvents. Examples include ionic liquids [2–4], inorganic supports [5–10] or under solvent-free conditions [11–17]. The solubility of ferrocenes has also been investigated in supercritical fluids [18], and some highly fluorinated ferrocenes have been synthesized for the fluorous phase technique [19]. Scheme 1 highlights four recent examples involving the clean synthesis of ferrocene derivatives. Sonification [20,21] and microwave radiation [22] have also been used in the clean synthesis of ferrocenes.

One of the current research goals within our group is the discovery and development of methods for the synthesis of ferrocenyl-containing molecules with the criteria being that the methods occur under mild conditions, are efficient providing high yields and high conversions and are environmentally friendly. This piece of work deals with the introduction of the ferrocenoyl group. The ferrocenoyl group is found in molecules proposed for a variety of applications. For example, it has been incorporated into medicinal molecules [23], liquid crystal molecules [24], molecules used as electrochemical sensors [25] and in molecules designed for anion recognition [26].

[1] The University of Port Elizabeth will in future form part of the Nelson Mandela Metropolitan University, Port Elizabeth, South Africa.

* Corresponding author. Tel.: +27415042823; fax: +27415042573.
E-mail address: Christopher.Imrie@upe.ac.za (C. Imrie).

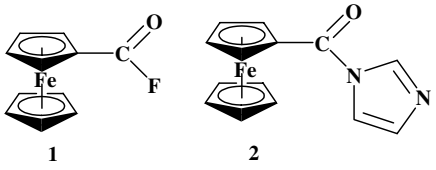
0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.08.015



Scheme 1.

Recently, we reported on the efficient syntheses of ferrocenoate esters from the reaction of ferrocenemonocarboxylic acid and phenols using the DCC/DMAP protocol in ionic liquid solvents [2]. In a follow-on paper, we reported on the synthesis of ferrocenylimines under solvent-free conditions [11]. From the viewpoint of green chemistry, a major drawback in the esterification work was the use of DCC since this gives rise to considerable quantities of *N*,*N*-dicyclohexylurea which is undesirable in terms of atom economy. One of the ways to avoid the use of DCC is to use an activated form of ferrocenemonocarboxylic acid. For this purpose, two reasonable choices are ferrocenoyl fluoride (**1**) and ferrocenoyl imidazolide (**2**). Both compounds are relatively stable solids at room temperature.

Ferrocenoyl chloride has been widely used as a source of the ferrocenoyl group despite the fact that it displays significant hydrolytic instability. Recently, Galow et al. [27] showed that ferrocenoyl fluoride (**1**) reacts with alcohols and amines in CH_2Cl_2 or THF to provide exceptionally high yields of esters and amides, respectively. Alternatively, Imrie et al. [28] have used ferrocenoyl imidazolide (**2**) as a useful source of the ferrocenoyl group. The work described in this paper discusses the reactions of **1** firstly in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) [29] secondly under solvent-free conditions [30].



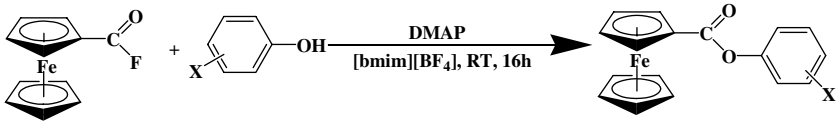
1 2

2. Results and discussion

Ferrocenoyl fluoride was synthesized by the reaction of ferrocenemonocarboxylic acid and cyanuric fluoride as described by Gallow et al. [27]. The compound was stored in a desiccator in the dark. Whilst the compound did not appear to be prone to any significant hydrolysis, it was susceptible to some kind of slow decomposition especially if left exposed to the atmosphere under ambient conditions. This type of behaviour is common to many ferrocenyl-containing molecules especially those in which strong electron-withdrawing groups are situated adjacent to the ferrocenyl group [31].

The reactions of ferrocenoyl fluoride with substituted phenols and *N*,*N*-dimethylaminopyridine (DMAP) in

Table 1
Yields of ferrocenyl esters from the reaction of ferrocenoyl fluoride and substituted phenols in [bmim][BF_4]



Entry	Substituent X	Yield (%)[a,b]
1	4-OCH_3	99
2	4-CH_3	98
3	4-H	94
4	4-Cl	99
5	4-NO_2	100
6	4-Br	60
7	4-CHO	80

[a] Yields are isolated ones.
[b] Esters were isolated and characterized by IR, NMR (^1H, ^{13}C) and high resolution mass spectroscopy.

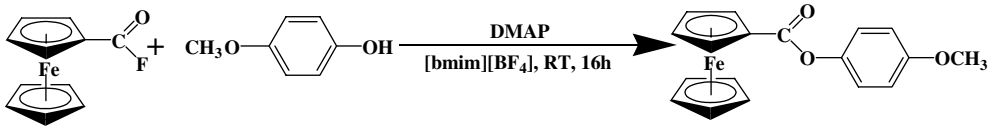
[bmim][BF_4] proceeded efficiently and provided excellent yields of ferrocenyl esters (Table 1). The ester products were easily extracted from [bmim][BF_4] using small quantities of diethyl ether. The conversions in all cases were very high which meant that the ionic liquid could be recovered at the end of each reaction in a reasonably clean state. For one of the esterification reactions, namely the reaction of ferrocenemonocarboxylic acid and 4-methoxyphenol in [bmim][BF_4], the solvent was recovered at the end of the first reaction and was then reused for the same reaction another four times. At the end of each reaction, the product was extracted with diethyl ether and the ionic liquid containing DMAP by-products was used directly in the following reaction. The results for the recycling reactions are shown in Table 2; the yields of the esters remained consistently high over the five runs. At the end of the series of experiments, the ionic liquid was analysed by ^1H and ^{13}C NMR spectroscopy to investigate its integrity. This was considered to be important in view of a recent publication by Aggarvaal et al. [32], which suggested that ionic liquids are not always benign solvents in reactions. The NMR spectra were identical to that of the starting material.

In order to expand the range of useful ferrocenoyl derivatives made from **1** in [bmim][BF_4], ferrocenoyl fluoride was reacted with other nucleophilic reagents and a summary of the reactions is provided in Scheme 2. The reactions of **1** with amines in [bmim][BF_4] provided amides in excellent yield. The reaction of **1** with thiophenol in [bmim][BF_4] provided the thioester (**3**).

Since one of our future aims is to study the reactivity and properties of free radicals in [bmim][BF_4] and other ionic liquids, we were eager to investigate the reactivity of **1** with *N*-hydroxy derivatives such as *N*-hydroxypyridine-2-thione, 3-hydroxy-4-methyl-2(3H)-thiazolethione and benzophenone oxime. Barton and co-workers [33] have utilized acyl derivatives of the first two molecules as a source of disciplined free radicals on mild photolysis. The reactions were conducted in the dark and all work-up procedures were carried out in a dark environment, since it was expected that the products would be light sensitive. The mixed anhydrides, compounds **4** and **5** were isolated in moderate yields and the compounds were identical to those prepared by us previously by a different route. Compounds **4** and **5** were extremely light sensitive and provided interesting photochemistry on mild photolysis in solution using a tungsten lamp. This chemistry will be published in a future piece of work. Reaction of **1** with benzophenone oxime in [bmim][BF_4] provided an excellent yield of the oxime ester **6**. This compound is a potential source of ferrocenoyloxyl free radicals ($FcCOO^{\cdot}$) since acyloxyl radicals have been generated from the photolysis of benzophenone oxime esters [34].

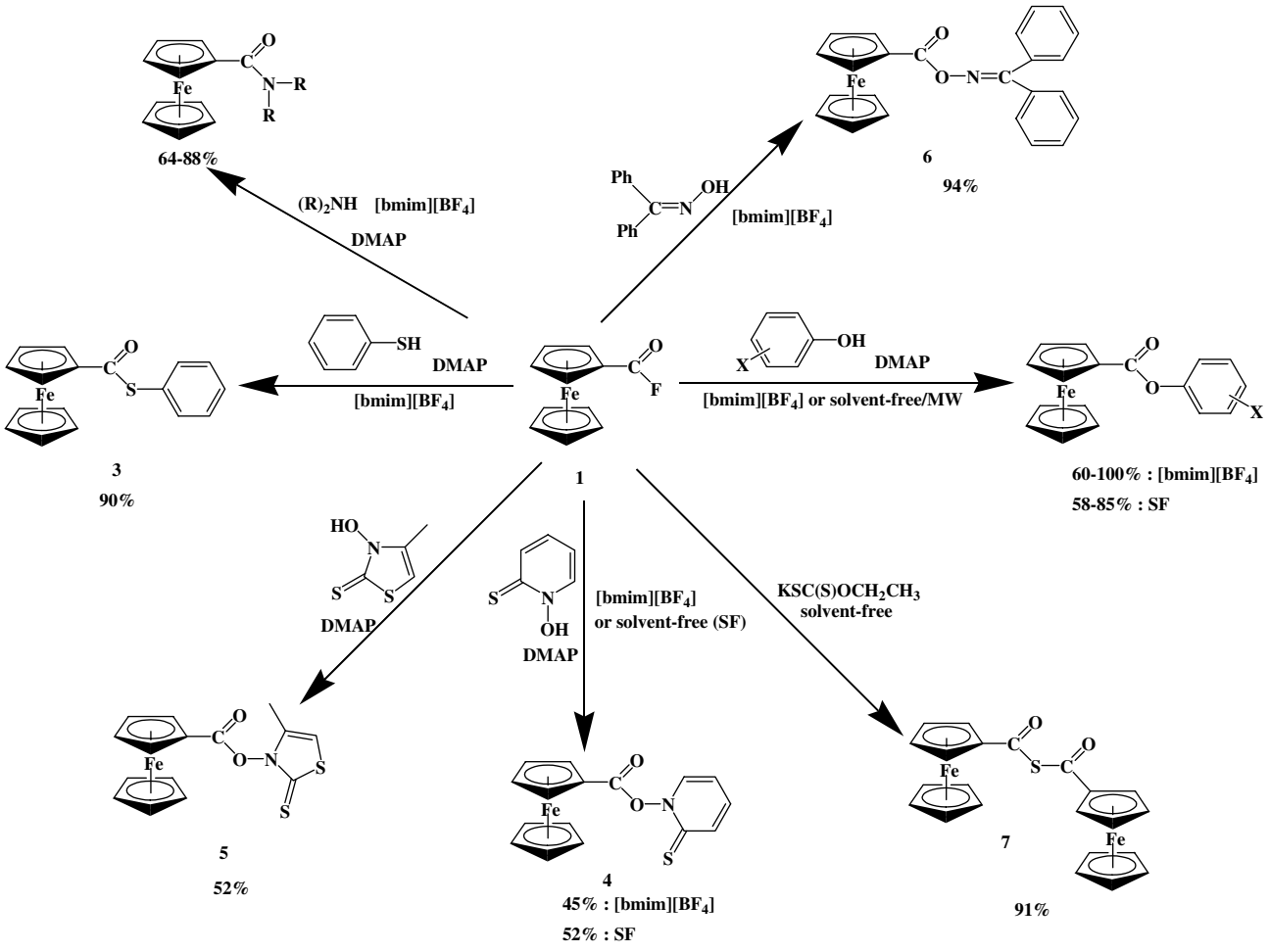
Following on from our recent success at using solvent-free conditions to synthesize ferrocenylimines [11], we were eager to investigate the solvent-free reactivity of **1** with a

Table 2
Results for recycling reactions (the reactions of ferrocenoyl fluoride with 4-methoxyphenol in [bmim][BF_4])



Reaction run	1	2	3	4	5
Yield of ester[a]	99	95	94	97	95

[a] Yields are isolated ones.

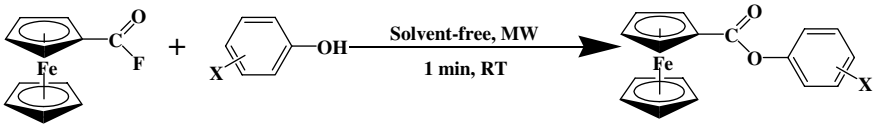


Scheme 2.

range of nucleophilic compounds. In the initial instance, attempts were made to react **1** with 4-methoxyphenol. The two compounds were ground in an open mortar for approximately three minutes but analysis indicated that no significant reaction had occurred. At this stage, the mixture was divided into two approximately equal parts. DMAP was added to the first part and a further period of grinding was carried out. Analysis of the paste indicated that some 4-methoxyphenyl ferrocenecarboxylate had formed but that the conversion was quite low. The second part of the mixture was subjected to irradiation by microwaves (1.5 min) and this provided an excellent yield of the ester with high conversion. A series of solvent-free microwave-promoted esterifications using ferrocenoyl fluoride and substituted phenols was then carried out and the results are provided in Table 3. The yields of esters are generally high. A reaction time of 1 min was found to be sufficient and the reaction could be run without DMAP highlighting the significant effect of the microwave radiation. Due to the sensitivity of the compounds **4** and **5**, microwave radiation was avoided in their solvent-free synthesis. Ferrocenoyl fluoride, the *N*-hydroxy derivative and DMAP were ground together under dark conditions and this provided modest yields of **4** and **5**. The solvent-free reaction of **1** with potassium-*O*-ethylxanthate gave an unexpected product, ferrocenoic thioanhydride (**7**). The expected product was $FcC(O)SC(S)OCH_2CH_3$ (**8**). Compound **8** was a desirable product, since it should act as an efficient source of ferrocenoyl free radicals (FcĊO). Zard and co-workers [35] have made widespread use of similar compounds to provide acyl radicals. The synthesis of **7** has been described previously by Katada et al. [36] and on that occasion **7** was made by the reaction of ferrocenoyl chloride and trimethylammonium ferrocenethiocarboxylate ($Fc(CO)SNMe_3$) in ether. Although there was no evidence for the formation of **8** in the solvent-free synthesis, it seems likely that **7** was formed in our work from the interaction of **1** and **8**.

There are various problems with the reactions just discussed in terms of their "green credentials." Firstly, ferrocenoyl fluoride is synthesized using cyanuric fluoride and this is a potentially hazardous chemical. Secondly, reactions take place with the liberation of hydrogen fluoride. In the ionic liquid or in a solvent such as THF, most of the hydrogen fluoride is removed by reaction with the base DMAP. The generation of hydrogen fluoride in the microwave-promoted solvent-free reactions poses more of a problem. Attempts to trap the hydrogen fluoride in the

Table 3
Yields of ferrocenyl esters from the microwave-promoted solvent-free reactions of ferrocenoyl fluoride and substituted phenols



Entry	Substituent X	Yield (%)[a,b]
1	4-OCH_3	79
2	3-OCH_3	78
3	4-CH_3	85
4	4-Bu^t	81
5	4-H	76
6	4-Cl	74
7	2-Cl	58
8	4-NO_2	65
9	4-Br	71

[a] Isolated yields based on ferrocenoyl fluoride.
[b] Esters were isolated and characterized by IR, NMR (^1H, ^{13}C) and high resolution mass spectroscopy.

microwave apparatus were thwarted by apparatus design and the small scale of the reaction.

3. Conclusion

Simple and convenient routes for the synthesis of ferrocenoyl derivatives have been described and involved either the reaction of nucleophilic compounds and DMAP with ferrocenoyl fluoride in [bmim][BF_4] or the solvent-free reactions of nucleophilic compounds with ferrocenoyl fluoride promoted by microwaves. The yields of the ferrocenoyl derivatives were in most cases excellent and purification was achieved with minimum use of solvent. Efficient trapping of hydrogen fluoride was achieved in [bmim][BF_4] but its generation remains a problem under solvent-free conditions.

4. Experimental

4.1. Purification and characterization of the materials

Silica gel 50 was used for column chromatography. Thin-layer preparative chromatography was carried out on plates using Merck silica gel 60 F_{254} (1.5 mm) as adsorbent. Melting points were recorded on an Electrothermal IA 900 series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series Fourier Transform IR spectrometer as KBr discs or as solutions in chloroform. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer as solutions in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on a VG70-SEQ/MSSMS2 spectrometer at the Cape Technikon. Recrystallizations were performed at room temperature. All solvents that required distillation were distilled directly into the reaction flask to be used, under nitrogen. The synthesis of [bmim][BF_4] and [bmim] [PF_6] has been described elsewhere [37]. Ferrocenemonocarboxylic acid was purchased from Strem (USA) and was used without further purification. The phenols and amines were recrystallized or distilled prior to use. *N*-Hydroxypyridine-2-thione was precipitated from an aqueous solution of its sodium salt with 6 M hydrochloric acid and washed with cold water and dried. Full characterization of the ferrocenyl esters and amides is provided in the supplementary material.

4.2. Synthesis of ferrocenoyl fluoride (*1*)

Ferrocenoyl fluoride was synthesised by the method reported by Galow et al. [27]. Quantity of ferrocenemonocarboxylic acid starting material (1.152 g, 5.00 mmol). The product was obtained as an orange crystalline solid **1** (0.974 g, 84%), M.p. 80–81 °C ([27] 68–69 °C); IR (KBr cm^{-1}) 1799, 1450, 1397, 1371, 1267, 1068, 995, 891, 818, 755, 698, 536, 484; ^1H NMR ($CDCl_3$) 4.88 (2H, t, $J = 1.9$ Hz, C_5H_4), 4.60 (2H, t, $J = 1.6$ Hz, C_5H_4), 4.33 (5H, s, C_5H_5); ^{13}C NMR($CDCl_3$) 165.7, 73.6, 71.7, 70.9, 69.8; *m/z* 232 (M^+, 92), 167 (45), 140 (57), 92 (100), 75 (12), 64 (14), 56 (10). Anal. Calc. for $C_{11}H_9FFeO$: [M^+] 231.99868; Found: [M^+], 231.99650.

4.3. Reactions of ferrocenoyl fluoride with phenols in [bmim][BF_4]: general method

[Bmim][BF_4] was deaerated by purging with nitrogen and was also subjected to three cycles of the freeze–thaw degassing technique. Ferrocenoyl fluoride (0.44 mmol), the substituted phenol (0.44 mmol) and *N*,*N*-dimethylaminopyridine (0.21 mmol) (DMAP) were added to degassed [bmim][BF_4] (6 cm^3) contained in a 25 cm^3 round-bottomed flask. Nitrogen was blown over the reaction before it was sealed and the reaction was then stirred at room temperature for 16 h. Stirring was stopped and the red-brown mixture was then extracted with diethyl ether (9×5 cm^3). The ether extracts were combined, washed with water and dried over anhydrous sodium sulfate. After removing the diethyl ether in vacuo, the residue was passed through

a short silica gel column. The products were eluted with hexane–diethyl ether (1:5) avoiding the use of undesirable chlorinated solvents.

4.4. Reaction of ferrocenoyl fluoride with 4-methoxyphenol in [bmim][BF_4]: general procedure for recycling experiments

Ferrocenoyl fluoride (0.44 mmol), DMAP (0.21 mmol), 4-methoxyphenol (0.44 mmol) and [bmim][BF_4] (6 cm^3) were placed in a 25 cm^3 RB flask. The flask was sealed and the mixture stirred at room temperature for 16 h. The reaction mixture was then extracted using diethyl ether (11×4 cm^3). The ether extracts were combined and washed twice with water and then dried over anhydrous sodium sulfate. After removing the ether in vacuo, the residue was passed through a short column of silica gel. Elution with hexane–diethyl ether (1:4) provided the product, 4-methoxyphenyl ferrocenecarboxylate. Fresh reactants were added to the recovered ionic liquid and the reaction was repeated in the same manner four more times. At the end of the fifth run, the ionic liquid (5.7 cm^3) was recovered. The recovered ionic liquid was analysed by ^{1}H NMR and gave a spectrum identical to pure [bmim][BF_4].

4.5. Reactions of ferrocenoyl fluoride with amines in [bmim][BF_4]: general method

Ferrocenoyl fluoride (0.44 mmol), the substituted amine (0.44 mmol) and DMAP (0.21 mmol) were added to [bmim][BF_4] (6 cm^3) in a 25 cm^3 round-bottomed flask. Nitrogen was blown over the reaction before it was sealed and the reaction was then stirred at room temperature for 16 h. Stirring was stopped and the mixture was then extracted with diethyl ether until the extracts were colourless. The ether extracts were combined, washed with water and dried over anhydrous sodium sulfate.

4.6. Reaction of ferrocenoyl fluoride with thiophenol: ferrocenoyl phenyl sulfide (**3**)

Ferrocenoyl fluoride (102 mg, 0.44 mmol), thiophenol (57 mg, 0.517 mmol) and DMAP (26 mg, 0.21 mmol) were added to [bmim][BF_4] (6 cm^3) contained in a 25 cm^3 round-bottomed flask. Nitrogen was blown over the reaction before it was sealed and the reaction was then stirred at room temperature for 16 h. Stirring was stopped and the red-brown mixture was then extracted with diethyl ether (8×5 cm^3). The ether extracts were combined, washed with water and dried over anhydrous sodium sulfate. After removing the diethyl ether in vacuo, the residue was passed through a short silica gel column. The products were eluted with hexane–diethyl ether (1:5) avoiding the use of undesirable chlorinated solvents. The product was obtained as a dark red solid (0.127 g, 90%) and was identified as ferrocenoyl phenyl sulfide (**3**). M.p. 108–109 °C, lit. 108–109 °C [28]; IR (KBr/cm^{-1}) 2950, 1664, 1614, 1438, 1239, 1044, 807; ^{1}H NMR ($CDCl_3$) 7.52 (2H, m, ArH), 7.48–7.44 (3H, m, ArH), 4.95 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.55 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.31 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 192.1, 135.4, 129.6, 129.5, 128.3, 79.2, 72.4, 71.1, 69.6; *m/z* 323 (17%), 322 ($M,^+$ 75), 230 (49), 228 (13), 214 (15), 213 (100), 211 (7), 186 (7) 185 (47), 129 (36), 121 (23); Anal. Calc. for $C_{17}H_{14}FeOS$: C, 63.4; H, 4.4%; [M^+], 322.0111. Found: C, 63.4; H, 4.3%; [M^+], 322.0117.

4.7. Reaction of ferrocenoyl fluoride with N-hydroxy derivatives

Ferrocenoyl fluoride (0.44 mmol), the *N*-hydroxy derivative (0.44 mmol) and DMAP (0.21 mmol) were added to [bmim][BF_4] (6 cm^3) in a 25 cm^3 round-bottomed flask. Nitrogen was blown over the reaction before it was sealed and the reaction was then stirred at room temperature for 16 h. Stirring was stopped and the mixture was then extracted with diethyl ether (9×5 cm^3). The ether extracts were combined, washed with water and dried over anhydrous sodium sulfate. After removing the diethyl ether in vacuo, the residue was passed through a short silica gel column. The products were eluted with hexane–diethyl ether avoiding the use of undesirable chlorinated solvents.

4.7.1. With N-hydroxypyridine-2-thione: N-ferrocenoyloxypyridine-2-thione (**4**)

Quantities. Ferrocenoyl fluoride (101 mg, 0.44 mmol), *N*-hydroxypyridine-2-thione (57 mg, 0.44 mmol), DMAP (21 mg, 0.172 mmol) and [bmim][BF_4] (6 cm^3). All operations in this reaction were carried out under dark conditions since the product is extremely light sensitive. The product was obtained as an orange solid and was identified as *N*-ferrocenoyloxypyridine-2-thione (67 mg, 45%), M.p. 145–146 °C; IR (KBr cm^{-1}) 3011, 1754, 1606, 1526, 1450, 1411, 1372, 1351, 1266, 1232, 1176, 1135, 1107, 1064, 1027, 986, 881, 845, 813, 766, 741, 533, 497; ^{1}H NMR ($CDCl_3$) 7.76 (1H, m, vinylic), 7.59 (1H, m, vinylic), 7.25 (1H, m, vinylic), 6.68 (1H, m, vinylic), 5.04 (2H, t, $J = 1.9$ Hz, C_5H_4), 4.62 (2H, t, $J = 1.9$ Hz, C_5H_4), 4.46 (5H, s, C_5H_5); *m/z* 339 (M^+, 100%), 323 (7), 248 (10), 247 (67), 230 (10), 213 (13), 199, (29), 185 (30), 166 (16), 134 (6), 130 (13), 129 (55), 121 (17), 103 (5), 92 (20), 83 (10), 78 (19), 69 (12), 56 (18), 51 (9), 39 (23); Anal. Calc. for $C_{16}H_{13}FeNO_2S$: [M^+], 339.00164. Found: [M^+], 339.00163.

4.7.2. With benzophenone oxime: benzophenone O-ferrocenylcarbonyloxime (**6**)

Quantities. Ferrocenoyl fluoride (102 mg, 0.44 mmol), benzophenone oxime (88 mg, 0.446 mmol), DMAP (25 mg, 0.205 mmol) and [bmim][BF_4] (6 cm^3). The product was obtained as a yellow solid identified as benzophenone *O*-ferrocenylcarbonyloxime (**6**) (0.169 g, 94%), M.p. 130–131 °C, (lit. [28] 130–131 °C); IR (KBr cm^{-1}) 3675, 3013, 2935, 2856, 1735, 1655, 1527, 1452, 1376, 1327, 1266, 1227, 1218, 1100, 1024, 985, 915; ^{1}H NMR ($CDCl_3$)

7.70–7.40 (10H, m, ArH), 4.60 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.36 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.10 (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$) 169.4, 164.8, 135.1, 133.3, 131.6, 129.9, 129.4, 129.1, 128.8, 128.6, 72.0, 70.5, 70.3, 69.5; *m/z* 409 (M^+, 100), 344 (88), 300 (61), 182 (68); Anal. Calc. for $C_{24}H_{19}FeNO_2$: C, 70.4; H, 4.7%; [M^+], 409.07652. Found: C, 70.8; H, 5.0%; [M^+], 409.07748.

4.8. Solvent-free reaction of ferrocenoyl fluoride with N-hydroxypyridine-2-thione

Ferrocenoyl fluoride (0.1009 g, 4.35×10^{-4} mol), *N*-hydroxypyridine-2-thione (0.0558 g, 4.39×10^{-4} mol) and DMAP (0.0209 g, 1.71×10^{-4} mol) were mixed and ground in an open mortar for 4 min. The mixture was analysed by FTIR and this confirmed the formation of a new product. The reaction mixture was taken up in a minimal amount of dichloromethane, and was then subjected to flash column chromatography using hexane–diethyl ether (1:3) as eluant. Blue coloured decomposition products were evident on the column. The eluate was concentrated under reduced pressure to give *N*-ferrocenoyloxypyridine-2-thione (**4**) as red-orange crystals (0.0860 g, 58%). The product was identical to that characterized in Section 4.7.1.

4.9. Solvent-free reaction of ferrocenoyl fluoride with 3-hydroxy-4-methyl-2(3H)-thiazolethione: N-ferrocenoyloxy-4-methyl-2(3H)-thiazolethione (5)

Ferrocenoyl fluoride (0.1003 g, 4.32×10^{-4} mol), 3-hydroxy-4-methyl-2(3H)-thiazolethione (0.0661 g, 4.49×10^{-4} mol) and DMAP (0.0169 g, 1.38×10^{-4} mol) were mixed and ground in an open mortar for 4 min. A dark-red paste formed. The reaction mixture was taken up in dichloromethane and subjected to column chromatography. Hexane–diethyl ether (2:1) eluted ferrocenoyl fluoride (0.0408 g). A second band was eluted with hexane–diethyl ether (1:2). A blue residue remained on the column. Removal of the solvent from the second band under reduced pressure gave *N*-ferrocenoyloxy-4-methyl-2(3H)-thiazolethione (**5**) as a red powder (0.0810 g, 52%), M.p. 133 °C decomp.; IR (KBr cm^{-1}) 3103, 3083, 1786, 1642, 1590, 1559, 1508, 1451, 1400, 1372, 1338, 1324, 1266, 1178, 1136, 1106, 1058, 1020, 991, 975, 871, 859, 827, 738, 724, 528; ^1H NMR ($CDCl_3$) 6.27 (1H, d, $J = 1.1$ Hz, vinylic), 5.04 (2H, t, $J = 1.7$ Hz, C_5H_4), 4.63 (2H, t, $J = 1.7$ Hz, C_5H_4), 4.48 (5H, s, C_5H_5), 2.19 (3H, d, $J = 1.1$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) 181.4, 168.4, 137.9, 102.8, 73.2, 71.9, 71.3, 70.6, 13.9; *m/z* 359 (M^+, 54%), 315 (9), 281 (6), 267 (21), 260 (26), 250 (26), 243 (7), 231 (23), 230 (97), 219 (17), 213 (86), 211 (6), 193 (7), 186 (17), 185 (60), 169 (16), 165 (9), 138 (46), 131 (57), 129 (64), 119 (32), 103 (7), 100 (11), 92 (13), 86 (41), 81 (9), 72 (11), 69 (100), 64 (8), 56 (26), 45 (33), 39 (21); Anal. Calc. for $C_{15}H_{14}FeNO_2S_2$: [M^+], 358.97371. Found: [M^+], 358.97302.

4.10. Solvent-free reaction of ferrocenoyl fluoride with potassium O-ethyl xanthate: ferrocenoic thioanhydride (7)

Ferrocenoyl fluoride (0.1004 g, 4.33×10^{-4} mol), potassium-*O*-ethyl xanthate (0.0647 g, 4.54×10^{-4} mol) and DMAP (0.0172 g, 1.41×10^{-4} mol) were mixed and ground in the dark. The mixture turned red after 1 min, formed a paste after 3.5 min and was ground for a further 2 min. The reaction mixture was taken up in dichloromethane and subjected to column chromatography. A red band was eluted with hexane–diethyl ether (1:3). The solvent mixture was removed under reduced pressure and this gave ferrocenoic thioanhydride (**7**) as red crystals (0.0909 g, 91%), M.p. 163 °C decomp. (lit. [36] 149–150 °C); IR (KBr cm^{-1}) 3448, 3107, 2931, 2362, 1761, 1692, 1652, 1565, 1477, 1435, 1376, 1044, 831, 780, 659, 494; ^1H NMR ($CDCl_3$) 4.92 (4H, t, $J = 1.9$ Hz, $2 \times C_5H_4$), 4.61 (4H, t, $J = 1.9$ Hz, $2 \times C_5H_4$), 4.36 (10H, s, $2 \times C_5H_5$); ^{13}C NMR ($CDCl_3$) 187.0, 80.1, 73.3, 71.1, 70.4; *m/z* 458 (M^+, 79 %), 442 (27), 366 (10), 350 (8), 306 (12), 274 (32), 272 (20), 214 (11), 213 (100), 209 (15), 186 (19), 185 (36), 181 (10), 131 (15), 129 (42), 119 (13), 92 (21), 69 (56); Anal. Calc. for $C_{22}H_{18}Fe_2O_2S$: [M^+], 457.97263. Found: [M^+], 457.97259. Crude ferrocenemonocarboxylic acid (0.0249 g) was stripped off the column with methanol.

4.11. Microwave-promoted reactions of ferrocenoyl fluoride with phenols under solvent-free conditions: general method

Ferrocenoyl fluoride (0.4 mmol) and a substituted phenol (0.4 mmol) were thoroughly mixed in a mortar. The mixture was subjected to microwave radiation for 1 min. The resulting melt was allowed to cool and was passed through a column of silica gel. Elution with hexane/ether (1:1) provided a band that upon removing the solvent gave the ferrocenoate ester. A small amount of ferrocenecarboxylic acid was removed from the column with methanol.

Acknowledgements

The authors thank the following persons for technical assistance: Mr. H. Marchand (UPE) for general technical assistance and Dr. P. Boshoff (formerly of the Cape Technikon, Cape Town) for the mass spectrometric analyses. The National Research Foundation (Pretoria) and the University of Port Elizabeth are gratefully acknowledged for funding the green chemistry project.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.08.015.

References

[1] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practise, Oxford, 1998.
[2] C. Imrie, E.R.T. Elago, C.W. McCleland, N. Williams, Green Chem. 4 (2002) 159.
[3] A. Stark, B.L. MacLean, R.D. Singer, J. Chem. Soc., Dalton Trans. (1999) 63.
[4] P.J. Dyson, Appl. Organomet. Chem. 16 (2002) 495.
[5] D. Villemin, M. Ricard, Synth. Commun. 17 (1987) 283.
[6] G. Cooke, H.M. Palmer, O. Schulz, Synthesis (1995) 1415.
[7] D. Villemin, A. BenAlloum, Phosphorus Sulfur Silicon 79 (1993) 33.
[8] E. Stankovic, P. Elecko, S. Toma, Chem. Pap. 50 (1996) 68.
[9] Y. Bai, J. Lu, H. Gan, Z. Wang, Z. Shi, Synth. React. Inorg. Metal-Org. Chem. 34 (2004) 1487.
[10] B.C. Ranu, U. Jana, A. Majee, Green Chem. (1999) 33.
[11] C. Imrie, V.O. Nyamori, T.I.A. Gerber, J. Organomet. Chem. 689 (2004) 1617.
[12] D. Villemin, B. Martin, M. Puciova, S. Toma, J. Organomet. Chem. 484 (1994) 27.
[13] W-Y. Liu, Q-H. Xu, B-H. Chen, Y-X. Ma, Synth. Commun. 32 (2002) 171.
[14] E. Stankovic, S. Toma, R. Van Boxel, I. Asselberghs, A. Persoons, J. Organomet. Chem. 637–639 (2001) 426.
[15] W-Y. Liu, Q-H. Xu, Y-X. Ma, Y-M. Liang, N-L. Dong, D-P. Guan, J. Organomet. Chem. 625 (2001) 128.
[16] D.I. Méndez, E. Klimova, T. Klimova, L. Fernando, S.O. Hernández, M.G. Martínez, J. Organomet. Chem. 679 (2003) 10.
[17] W-Y. Liu, Q-H. Xu, Y-M. Liang, B-H. Chen, W-M. Liu, Y-X. Ma, J. Organomet. Chem. 637–639 (2001) 719.
[18] C.M. Cowey, K.D. Bartle, M.D. Burford, A.A. Clifford, S. Zhu, N.G. Smart, N.D. Tinker, J. Chem. Eng. Data 40 (1995) 1217.
[19] J. Kvíčala, T. Bříza, O. Paleta, K. Auerová, J. Čermák, Tetrahedron 58 (2002) 3847.
[20] M. Woltersdorf, R. Kranich, H-G. Schmalz, Tetrahedron 53 (1997) 7219.
[21] S-J. Ji, Z-L. Shen, D-G. Gu, S-Y. Wang, J. Organomet. Chem. 689 (2004) 1843.
[22] B.F. Bonini, C. Femoni, M. Comes-Franchini, M. Fochi, G. Mazzanti, A. Ricci, G. Varchi, Synlett (2001) 1092.
[23] E.I. Edwards, R. Epton, G. Marr, J. Organomet. Chem. 107 (1976) 351;
I. Bediako-Amoa, R. Silerova, H-B. Kraatz, Chem. Commun. (2002) 2430.
[24] C. Imrie, P. Engelbrecht, C. Loubser, C.W. McCleland, Appl. Organomet. Chem. 15 (2001) 1.
[25] J.D. Carr, L. Lambert, D.E. Hibbs, M.B. Hursthouse, K.M.A. Malik, J.H.R. Tucker, Chem. Commun. (1997) 1649.
[26] P.D. Beer, Chem. Commun. (1996) 689.
[27] T.H. Galow, J. Rodrigo, K. Cleary, G. Cooke, V.M. Rotello, J. Org. Chem. 64 (1999) 3745.
[28] C. Imrie, L. Cook, D.C. Levendis, J. Organomet. Chem. 637–639 (2001) 266.
[29] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003.
[30] K. Tanaka, Solvent-free Organic Synthesis, Wiley-VCH, Weinheim, 2003.
[31] C. Imrie, Appl. Organomet. Chem. 9 (1995) 75.
[32] V.K. Aggarwal, I. Emme, A. Mereu, Chem. Commun. (2002) 1612.
[33] D.H.R. Barton, D. Crich, W.B. Motherwell, J. Chem. Soc., Chem. Commun. (1983) 939;
D.H.R. Barton, D. Crich, W.B. Motherwell, Tetrahedron 41 (1985) 3901.
[34] M. Hasebe, K. Kogawa, T. Tsuchiya, Tetrahedron Lett. 25 (1984) 3887;
M. Hasebe, T. Tsuchiya, Tetrahedron Lett. 28 (1987) 6207.
[35] B. Quiclet-Sire, S.Z. Zard, Pure Appl. Chem. 69 (1997) 645.
[36] T. Katada, M. Nishida, S. Kato, M. Mizuta, J. Organomet. Chem. 129 (1977) 189.
[37] P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. De Souza, J. Dupont, Polyhedron 15 (1996) 1217.