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# Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

Acylation of Ferrocene and a 1,1'-Diphosphaferrocene with Acyl Trifluoroacetates in the Presence of Trifluoromethanesulfonic (Triflic) Acid or Some Metal Triflates

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Version of record first published: 16 Aug 2006.

To cite this article: Damian Plażuk & Janusz Zakrzewski (2004): Acylation of Ferrocene and a 1,1'-Diphosphaferrocene with Acyl Trifluoroacetates in the Presence of Trifluoromethanesulfonic (Triflic) Acid or Some Metal Triflates, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 34:1, 99-107

To link to this article: <u>http://dx.doi.org/10.1081/SCC-120027243</u>

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SYNTHETIC COMMUNICATIONS<sup>®</sup> Vol. 34, No. 1, pp. 99–107, 2004

# Acylation of Ferrocene and a 1,1'-Diphosphaferrocene with Acyl Trifluoroacetates in the Presence of Trifluoromethanesulfonic (Triflic) Acid or Some Metal Triflates

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### ABSTRACT

Ferrocene and 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene undergo efficient acylation by acyl trifluoroacetates (prepared in situ from carboxylic acids and trifluoroacetic anhydride) in the presence of an excess of trifluoromethanesulfonic acid or catalytic amounts (10% mol.) of its ytterbium or hafnium salts.

*Key Words:* Ferrocene; Friedel-Crafts acylation; Triflic acid; Metal triflate; 1,1'-Diphosphaferrocene.

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Continuously growing applications of substituted ferrocenes in modern chemical, biological and material sciences,<sup>[1,2]</sup> including chiral catalysis,<sup>[3–5]</sup> red-ox active polymers and dendrimers,<sup>[6–9]</sup> nonlinear optical materials,<sup>[10–12]</sup> molecular electronic devices,<sup>[13,14]</sup> biosensors,<sup>[15–18]</sup> components of complex photochemical systems,<sup>[19–21]</sup> drugs <sup>[22]</sup> etc. largely stimulated development of synthetic methods enabling introduction to this metallocene desired carbon chains and/or functional groups. The intrinsic high nucleophilic reactivity of ferrocene<sup>[1,2,23]</sup> makes Friedel–Crafts acylation, hydroxyalkylation and alkylation (or alkenylation) a particularly attractive method for synthesis of substituted ferrocene.<sup>[23–28]</sup>

In recent years a significant progress in the Friedel-Crafts chemistry of arenes was achieved. It involves inter alia the discovery of the catalysis by metal trifluoromethanesulfonates (triflates),<sup>[29]</sup> superacids<sup>[30–32]</sup> and the use of mixed anhydrides such as acyl triflates<sup>[33,34]</sup> and acyl trifluoroacetates<sup>[35,36]</sup> as electrophilic reagents. However, up to now only a few works have been devoted to introduction of these achievements to the ferrocene chemistry in order to simplify synthetic procedures and to make them milder, more efficient and eco-friendly. In most cases acid chlorides or anhydrides and AlCl<sub>3</sub> or BF<sub>3</sub> are used in ferrocene acylation<sup>[37]</sup> (although an interesting electrochemical generation of the acylating agent was recently reported<sup>[38]</sup>). Roberts and Wells reported acylation of ferrocene, 3,4-dimethylphosphaferrocene and 3,3',4,4'tetramethyl-1,1'-diphosphaferrocene with acid anhydrides in the presence of triflic acid (TfOH).<sup>[39]</sup> They found that the use of this protic acid in place of a classical Lewis acid (AlCl<sub>3</sub>) led to better yields of acylated products, especially for less stable heteroferrocenes. A paper by Galli<sup>[40]</sup> briefly mentioned that ferrocene can be acetylated by acetyl trifluoroacetate in the presence of 85% H<sub>3</sub>PO<sub>4</sub>, but more systematic study on this system are lacking. More recently Ranu et al.<sup>[41]</sup> described efficient and selective monoacylation of ferrocene with acyl trifluoroacetates (prepared in situ from carboxylic acids and trifluoroacetic anhydride, TFAA) on the solid phase of alumina.

In this paper we report the acylation of ferrocene (1) by acyl trifluoroacetates in the presence of triflic acid, or catalytic amounts of metal triflates such as ytterbium triflate Yb(OTf)<sub>3</sub> and hafnium triflate Hf(OTf)<sub>4</sub> (Sch. 1). As there is an increasing interest in development of synthetic chemistry of the group 15 elements heteroferrocenes<sup>[42–44]</sup> we have tested applicability of our method in this field using 3,3',4,4',-tetramethyl-1,1'-diphosphaferrocene (2), a stable and readily available heteroferrocene, which is known to undergo Friedel–Crafts acylation by acyl chlorides or anhydrides in the presence of AlCl<sub>3</sub>.<sup>[45]</sup>

When a carboxylic acid RCOOH is mixed with a stoichiometric amount of TFAA an acyl trifluoroacetate, RCOOCOCF<sub>3</sub>, is formed. Acyl trifluroacetates are reactive electrophiles in aromatic acylation, but usually require



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Scheme 1.

strong acid catalysis (trifluoroacetic acid formed in the reaction between RCOOH and TFAA may be not sufficiently strong.<sup>[35,36]</sup> We have found that ferrocene is slowly acetylated by a 1:1 mixture of acetic acid and TFAA (1.0 molar equivalent) in dichloromethane at r.t. The isolated yield of acetylferrocene was low (8% after 1 h, 12% after 4 h and 9% after 20 h). However, in the presence of triflic acid (4.0 molar equivalents) the acetylation proceeded smoothly and after 1 h acetylferrocene was isolated in 92% yield. In the absence of TFAA no reaction was observed. The results obtained for acylation of ferrocene and 3,3',4,4'-tetramethyldiphosphaferrocene with acyl triflates (RCOOH/TFAA) in the presence of triflic acid are gathered in Table 1 (Method A). The best yields in this method (92-97%) in the case of acylation of ferrocene) were obtained for simple aliphatic acids. Aromatic acids proved slightly less efficient. Acylation of 2 proceeds with lower yields that acylation of ferrocene. The yield of 2-benzoyl-3,3',4,4',-tetramethyl-1,1'-diphosphaferrocene is comparable with that reported earlier, using (PhCO)<sub>2</sub>O/TfOH,<sup>[40]</sup> whereas lower yield was obtained for acetylation. In no case was formation of diacylated products observed. This may be due to the extensive protonation of

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Metallocene	Method <sup>a</sup>	Product (R)	Yield, %
1	А	<b>3a</b> (Me)	92
	В	<b>3a</b> (Me)	66 (90) <sup>b</sup>
	С	<b>3a</b> (Me)	54
	А	<b>3b</b> (Et)	92
	В	<b>3b</b> (Et)	74
	А	<b>3c</b> ( <i>t</i> -Bu)	97
	А	<b>3d</b> (Ph)	78
	В	<b>3d</b> (Ph)	12
	С	<b>3d</b> (Ph)	29
	А	<b>3e</b> ( <i>p</i> -MeOPh)	69
	В	<b>3e</b> ( <i>p</i> -MeOPh)	31
	А	<b>3f</b> (PhCH <sub>2</sub> )	72
2	А	<b>4a</b> (Me)	58
	В	<b>4a</b> (Me)	48
	С	<b>4a</b> (Me)	70
	А	<b>4b</b> (Ph)	73
	С	<b>4b</b> (Ph)	63

*Table 1.* Acylation of ferrocene and 3,3',4,4',-tetramethyl-1,1'-diphosphaferrocene.

<sup>a</sup>A: RCOOH/TFAA/Metallocene/TfOH 1:1:1:4; B: RCOOH/ TFAA/Metallocene/Yb(OTf)<sub>3</sub> 1:1:1:0.1; C: RCOOH/TFAA/ Metallocene/Hf(OTf)<sub>4</sub> 1:1:1:0.1.

<sup>b</sup>Based on reacted 1.

acyl metallocenes in strongly acidic reaction medium, lowering their reactivity towards electrophiles.<sup>[40]</sup>

In a series of works Kobayashi et al.<sup>[29]</sup> have shown that rare earth metal triflates and scandium- or hafnium-triflate catalyze acylation of arenes by acid chlorides or anhydrides. We have therefore decided to look whether triflic acid in the Method A can be replaced by a catalytic amount of Yb(OTf)<sub>3</sub> or Hf(OTf)<sub>4</sub>. The results obtained for reaction of the RCOOH-TFAA (1:1) system with ferrocene and 3,3',4,4',-tetramethyl-1,1'-diphosphaferrocene in dichloromethane in the presence of 10% mol of the triflate are shown in Table 1 (Methods B and C for the ytterbium and hafnium salt, respectively).

These results show efficient catalysis by both triflates. Generally, in the case of ferrocene Methods B and C give moderate to good yields of acylated products (although lower than those obtained using Method A) for aliphatic acids and only poor yields for aromatic acids. The hafnium salt proved more efficient than its ytterbium counterpart for benzoylation and less efficient for acetylation (Table 1). In the case of the acetylation of **2** the hafnium triflate-



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catalyzed reaction proceeds more efficiently than the triflic acid-catalyzed reaction.

According to earlier works,<sup>[29–36]</sup> our acylating systems could offer an opportunity of the recycling of TFAA (as trifluoroacetic acid, TFA), TfOH (as the barium salt) and metal triflates. However, working at a one milimole-scale we have not tested this opportunity. A considerable advantage of our method is also the use of carboxylic acids instead of less readily available acid chlorides and anhydrides.

In conclusion, we have described novel and efficient acylation reactions of ferrocene and a 1,1'-diphosphaferrocene using carboxylic acids and TFAA in the presence of triflic acid or a metal triflate.

### EXPERIMENTAL

### General

Dichloromethane was distilled over calcium hydride. The reactions described here do not require an inert gas atmosphere and were carried out in air with protection against humidity. Ferrocene was purchased from Aldrich and used without prior purification. Compound **2** was prepared according to the literature procedure.<sup>[46]</sup> Other reagents and solvents were obtained from Aldrich and used as received.

General procedure for acylation of **1** and **2**: A solution of a carboxylic acid (1.0 mmol) and TFAA (1.0 mmol) in dichloromethane (5 mL) was stirred at r.t. for 1 h. **1** or **2** (1.0 mmol) and triflic acid (4.0 mmol, Method A) or a metal triflate (0.1 mmol, Method B and C) were then added, and the mixture was stirred 1 h. After quenching with water, extraction with dichloromethane the product was isolated by column chromatography (silicagel, chloroform) as an orange-red band which followed the yellow band containing a small amount of unreacted **1** or **2**. The products were identified by spectral comparison with the authentic samples.<sup>[37,45,47]</sup>

Acetylferrocene (3a). M.p.  $85-86^{\circ}$ C (Lit.<sup>[37]</sup>  $86-87^{\circ}$ C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.77 (t, J = 1.8 Hz, 2H, H2 and H5), 4.55 (t, J = 1.8 Hz, 2H, H3 and H4), 4.19 (s, 5H, unsubst. Cp), 2.37 (s, 3H, Me). IR (KBr):  $\nu$ (CO) 1660 cm<sup>-1</sup>.

**Propionylferrocene** (**3b**). M.p.  $38-39^{\circ}$ C (Lit.<sup>[37]</sup>  $34-36^{\circ}$ C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.78 (t, J = 1.8 Hz, 2H, H2 and H5), 4.45 (t, J = 1.8 Hz, 2H, H3 and H4), 4.19 (s, 5H, unsubst. Cp), 2.69 (q, J = 7.5 Hz, 2H, CH<sub>2</sub>), 1.17 (t, J = 7.5 Hz, 3H, CH<sub>3</sub>). IR (KBr):  $\nu$ (CO) 1660 cm<sup>-1</sup>.

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**Pivaloylferrocene (3c)**. M.p. 92–93°C (Lit.<sup>[23]</sup> 92°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.84 (t, J = 1.8 Hz, 2H, H2 and H5), 4.46 (t, J = 1.8 Hz, 2H, H3 and H4), 4.19 (s, 5H, unsubst. Cp), 1.33 (s, 9H, *t*-Bu). IR (KBr):  $\nu$ (CO) 1655 cm<sup>-1</sup>.

**Benzoylferrocene** (3d). M.p.  $105-107^{\circ}$ C (Lit.<sup>[37]</sup>  $105-107^{\circ}$ C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.5–7.9 (m, 5H, Ph), 4.90 (t, J = 1.8 Hz, 2H, H2 and H5), 4.55 (t, J = 1.8 Hz, 2H, H3 and H4), 4.18 (s, 5H, unsubst. Cp), IR (KBr):  $\nu$ (CO) 1664 cm<sup>-1</sup>.

(4-Methoxybenzoyl)ferrocene (3e). M.p. 74–75°C (Lit.<sup>[37]</sup> 74–76°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.93 (d, J = 8.6 Hz, aromatic), $\delta$ ): 7.02 (d, J = 8.6 Hz, aromatic), 4.84 (t, J = 1.8 Hz, 2H, H2 and H5), 4.50 (t, J = 1.8 Hz, 2H, H3 and H4), 4.12 (s, 5H, unsubst. Cp). IR (KBr):  $\nu$ (CO) 1652 cm<sup>-1</sup>.

(Phenylacetyl)ferrocene (3f). M.p.  $128-130^{\circ}$ C (Lit.<sup>[23]</sup>  $130^{\circ}$ C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.26–7.35 (m, 5H, Ph), 4.89 (t, J = 1.8 Hz, 2H, H2 and H5), 4.51 (t, J = 1.8 Hz, 2H, H3 and H4), 4.12 (s, 5H, unsubst. Cp), 3.98 (s, 2H, CH<sub>2</sub>). IR (KBr):  $\nu$ (CO) 1658 cm<sup>-1</sup>.

**2-Acetyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene (4a)**. M.p. 68–70°C (Lit.<sup>[45]</sup> ~71°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.00 (d, J = 36.2 Hz, 1H, H5), 3.71 (d, J = 36.0 Hz, 2H, H2' and H5'), 2.28 (d, J = 2.9 Hz, 3H, acetyl), 2.39 (s, 3H, Me), 2.10 (s, 3H, Me), 2,06 (s, 3H, Me); 2.00 (s, 3H, Me). IR (KBr):  $\nu$ (CO) 1652 cm<sup>-1</sup>.

**2-Benzoyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene** (4b). M.p. 66–68°C (Lit.<sup>[45]</sup> ~70°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.3–7.6 (m, 5H, Ph), 3.94 (d, J = 36.2 Hz, 1H, H5), 3.63 (d, J = 36.0 Hz, 2H, H2' and H5'), 2.30 (s, 3H, Me), 2.15 (s, 3H, Me), 2,08 (s, 3H, Me); 1.98 (s, 3H, Me). IR (KBr):  $\nu$ (CO) 1642 cm<sup>-1</sup>.

### ACKNOWLEDGMENT

We thank University of Lodz for financial support of this work (Grant 505/471).

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Received in Poland April 27, 2003

