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# Carboxylation of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene with $CO_2$ in the presence of $AlCl_3$

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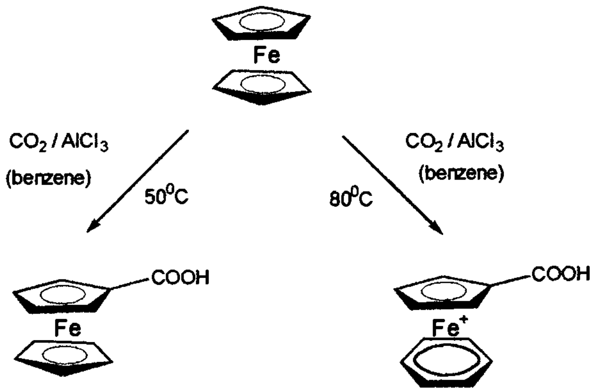
**Abstract**

3,3′,4,4′-Tetramethyl-1,1′-diphosphaferrocene (**1**) is carboxylated by $CO_2$ in the presence of $AlCl_3$ at ambient pressure to afford 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene-2-carboxylic acid (**2**) in moderate (up to 30%) yield. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* 1,1′-Diphosphaferrocene; Carboxylation; Electrophilic substitution

## 1. Introduction

Ferrocene reacts in the presence of aluminum chloride with a rather weak electrophile, carbon dioxide, to afford ferrocenecarboxylic acid (Scheme 1) [1,2]. The reaction is carried out in benzene at 50 °C. At a higher temperature (80 °C) the subsequent replacement of the unsubstituted cyclopentadienyl ligand by benzene takes place [2].

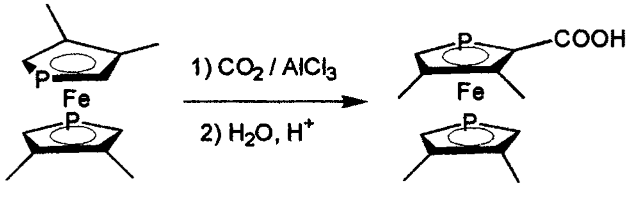


Scheme 1.

1,1′-Diphosphaferrocene, a phosphorous analog of ferrocene, displays high reactivity in Friedel–Crafts reactions [3–5]. This reactivity has been studied mostly using 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**1**), which is more readily available and more stable than the unsubstituted, 1,1′-diphosphaferrocene. It has been found that **1** can be mono- and di-acetylated by $CH_3COCl–AlCl_3$ [3] and reacts with ethyl chloroformate–$AlCl_3$ [6] to afford ethyl ester of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene-2-carboxylic acid.

We thought that it would be interesting to see if **1** can be carboxylated by $CO_2–AlCl_3$. This reaction would open a cheap, one-step way to 3,3′,4,4′-tetramethyl-1,1′-diphospha-ferrocene-2-carboxylic acid, otherwise accessible only via hydrolysis of the above-mentioned ethyl ester [6].

In this Note we report that **1** does react with $CO_2$ in the presence of $AlCl_3$ to afford the corresponding acid **2** (Eq. 1; **1** and **2** shown in conformations established by X-ray crystallography [3,7]) in moderate yields.



**1** **2**

(1)

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Table 1
Carboxylation of **1** with $CO_2$ at ambient temperature and pressure

| Solvent | Reaction time (h) | $AlCl_3$ (mol per mol of **1**) | Recovered **1** (%) | Yield of **2** (%) |
|---|---|---|---|---|
| $CH_2Cl_2$ | 2 | 1 | 75 | 5 |
| | 2 | 2 | 61 | 21 |
| | 2 | 4 | 75 | 6 |
| | 2 | 6 | 56 | $<2$ |
| $CS_2$ | 3 | 1 | 65 | 14 |
| | 3 | 1.5 | 57 | 30 |
| | 3 | 2 | 61 | 15 |
| | 3 | 4 | 50 | $<2$ |

The reaction of **1** with $CO_2$–$AlCl_3$ was carried out at ambient temperature and pressure in three solvents: benzene, dichloromethane and carbon disulfide. No formation of **2** was observed in the first solvent. The influence of the reaction conditions on the yield of isolated **2** is shown in Table 1.

In all reactions considerable amounts ($>50\%$) of unreacted **1** were recovered. The prolongation of the reaction time beyond the values indicated in Table 1 did not push the reaction to completion, but only decreased the yields of isolated **2**. The amount of $AlCl_3$ is of critical importance and the best yields of **2** were obtained using 1.5–2 molar equivalents of this Lewis acid. Larger amounts of $AlCl_3$ led to decomposition of both **1** and **2**. The best yield of **2** (30%) was obtained in reaction carried out in $CS_2$ in the presence of 1.5 equivalents of $AlCl_3$. This value is somewhat higher than the overall yield of the two-step procedure reported by Mathey et al. (22%) [6], and our method is simpler and cheaper.

It is also worth noting that because of the sensitivity of the phosphorus atoms in **1** to nucleophilic attack by RLi [4,5], this metallocene cannot be lithiated and therefore a way to **2** through reaction of the lithio derivative of **1** with $CO_2$ (the method currently used to obtain ferrocenecarboxylic acid from ferrocene) is not accessible in this case.

The racemic **2** has recently been resolved into enantiomers [8], and transformed into readily separable diastereomeric amides having both planar and central chirality [9]. In our opinion it can be used as a precursor of planar chiral ligands for asymmetric catalysis.

## 2. Experimental

Complex **1** was obtained according to the earlier described procedure [10].

### 2.1. Carboxylation of 1

To a magnetically stirred solution of **1** (278 mg, 1 mmol) in $CH_2Cl_2$ or $CS_2$ (5 ml) an appropriate amount of $AlCl_3$ was added and then dry $CO_2$ was bubbled slowly through 2–3 h. The reaction mixture was then poured onto 2 N HCl, extracted with dichloromethane, dried ($Na_2SO_4$) and evaporated to dryness. Column chromatography (silicagel/chloroform) afforded unreacted **1** followed by a red band of **2**. Dark red crystalline solid. IR (KBr, $cm^{-1}$): 1675. $^1$H-NMR (200 MHz, $CDCl_3$, $\delta$ [ppm]); 4.16 (d, $^2J_{P-H} = 36.0$ Hz, 1H, H-5); 3.89 (dd, $^2J_{P-H} = 36.0$ Hz, $^4J_{H-H} = 4.0$ Hz, 1H, H-2′ or H-5′); 3.65 (dd, $^2J_{P-H} = 36.0$ Hz, $^4J_{H-H} = 4.0$ Hz, 1H, H-2′ or H-5′); 2.40, 2.17, 2.09 and 2.07 (singlets, each 3H, methyls). $^{31}$P-NMR (81 MHz, $^1$H decoupling, $CDCl_3$, $\delta$ [ppm]): $-52.5$ (d, $J_{P-P} = 7.0$ Hz) and $-66.9$ (d, $J_{P-P} = 7.0$ Hz). These spectra are in full accord in those reported for **2** [6]. TLC properties of this compound were identical with those of an authentic sample [6].

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