Available online at www.sciencedirect.com
ScienceDirect
Inorganica Chimica Acta 361 (2008) 2172–2175
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Note

Deamination of 1-aminoethylferrocene and the crystal structure of ethenylferrocene

C. John McAdam *, Brian H. Robinson, Jim Simpson

Department of Chemistry, University of Otago, P.O. 56, Dunedin 9001, New Zealand

Received 7 August 2007; received in revised form 9 October 2007; accepted 21 October 2007
Available online 1 November 2007

Abstract

Ethenylferrocene, $C_{12}H_{12}Fe$, was an unexpected product of the thermolysis of 1-aminoethylferrocene in a melt reaction with naphthalene-2,3-dicarboxylic acid. It was characterized by single crystal X-ray diffraction which revealed that the cyclopentadiene rings are slightly staggered and the ethenyl substituent lies approximately in the plane of the substituted cyclopentadiene ring. In the crystal structure C–H···π interactions link molecules into parallel rows.

Keywords: Deamination; Ferrocene; X-ray crystal structure

1. Introduction

It is more than fifty years since the first reported synthesis of ethenylferrocene (**1**) by Arimoto and Haven [1]. The literature now contains thousands of papers utilising this versatile small molecule and covering its extensive polymer chemistry. We report here the crystal structure of this fundamental organometallic building block and the unconventional synthesis that led to its preparation.

2. Results and discussion

N-Ferrocenylnaphthalimides have been prepared by the reaction of 1,8-naphthalic anhydrides with ferrocenyl amines or, in the case of 2,3-napthalimides, by the direct reaction between the amines and naphthalene-2,3-dicarboxylic acid [2]. The latter synthesis is based on the well known synthetic strategy for *N*-phenyl-2,3-naphthalimides from naphthalene-2,3-dicarboxylic acid and a four molar excess of aniline, at elevated temperature [3].

Using this strategy to prepare *N*-1-(ferrocenyl)ethyl-2,3-naphthalimide (**2**) from 1-aminoethylferrocene (Scheme 1) [2] led also to the isolation of ethenylferrocene, **1** in yields of up to 50% (based on excess starting amine).

Ethenylferrocene has been previously prepared by a variety of routes. The seminal work involved dehydration of ferrocenylethanol at elevated temperature with Al_2O_3 [1].

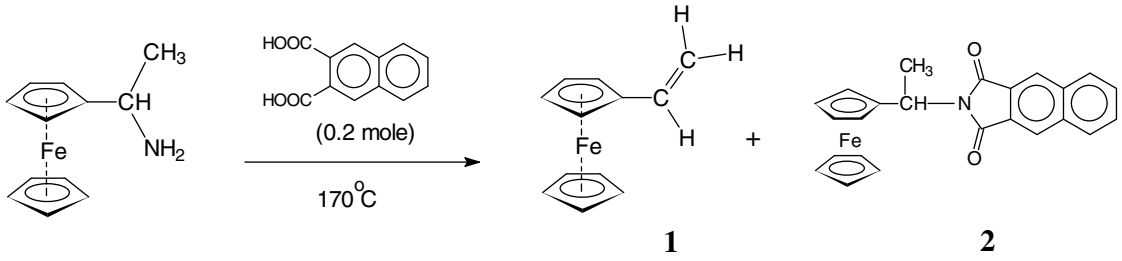
Other thermal preparations utilise acetylferrocene [4] and formylferrocene [5], the latter being our preferred synthetic route. A methyl iodide quaternisation of the amine in Fc–CHMe–NMe_2, and a multistep synthesis from Fc–CH_2–NMe_2 also lead to the preparation of **1** [6,7]. Complementary to this, a reaction in the reverse direction provides convenient synthesis of (2-aminoethyl)ferrocenes from ethenylferrocene and lithium amides [8].

To our knowledge this is the first report of an acid-catalysed deamination for the preparation of **1**. The proposed course of the reaction leading to the observed product is shown in Scheme 2, with a driving force provided by the intermediate formation of an α-ferrocenyl carbenium ion, well known for its particular stability [9–11], following protonation and deamination of the starting material.

The structure of the unexpected product **1** had, surprisingly, not been reported previously and was investigated by single crystal X-ray diffraction (Fig. 1).

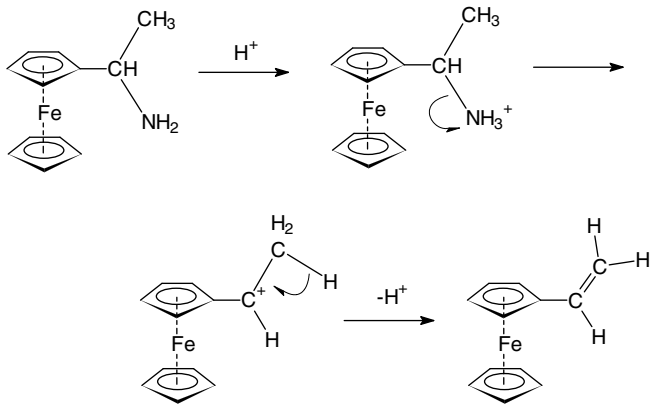
* Corresponding author.
E-mail address: mcadamj@alkali.otaga.ac.nz (C.J. McAdam).

0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.10.035



1 2

Scheme 1.



Scheme 2.

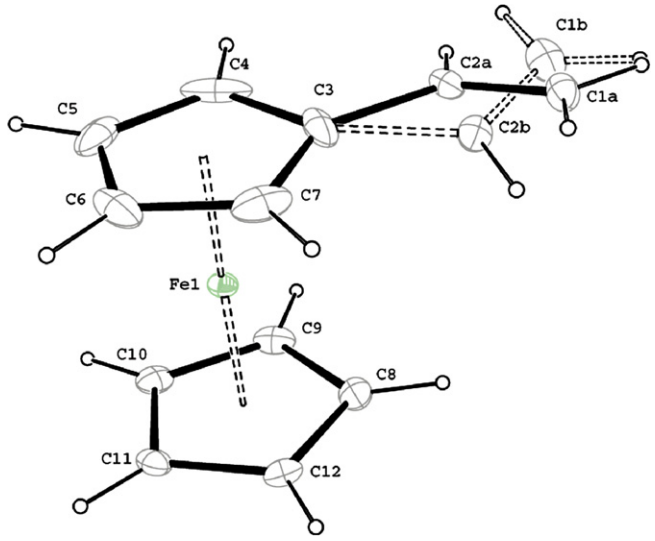


Fig. 1. The molecular structure of **1** with atom labels and 50% probability displacement ellipsoids for non-H atoms. Bonds to atoms of the minor disorder component are drawn as dashed lines.

The cyclopentadienyl rings of the ferrocene vary somewhat from an eclipsed orientation, with a mean cyclopentadienyl twist angle of 10.0(2)°; the relatively high uncertainty in this value may reflect the possible unresolved disorder in the vinyl substituted cyclopentadienide ring. The dihedral angle between the Cp ring planes is 2.1(2)°. The ethenyl substituent is disordered over two sites (a and b) but each component lies approximately in the plane of the C3···C7 cyclopentadiene ring, with the maximum deviation 0.158(5) Å for C1a. A search of the Cambridge database [12] (V 5.28 to January 2007) reveals 11 other ethenylferrocene complexes [13–16]. The C=C distances observed here in Table 1 for the two disorder components are similar to those in other ethenylferrocene compounds (mean C=C 1.32(3) Å).

In the crystal structure C11–H11···Cg1^{i} (C11···Cg1^{i} = 3.6474(18) Å; C11–H11···Cg1^{i} = 136.4°; i = x, $-y-1/2$, $z-1/2$) and C2a–H2a···Cg2^{ii} interactions (C2a···Cg2^{ii} = 3.881(2) Å; C2a—H2a···Cg2^{ii} = 170.4°; ii = x, $1/2-y$, $1/2+z$) [17] link adjacent molecules into parallel rows along diagonals of the *bc* plane, Fig. 2, Table 2 (Cg1 and Cg2 are the centroids of the C3···C7 and C8···C12 cyclopentadienyl rings, respectively).

3. Experimental

1-Aminoethylferrocene (1.15 g, 5 mmol) was added to naphthalene-2,3-dicarboxylic acid (0.22 g, 1 mmol) and the mixture heated at 170 °C for 15 min. Orange **1** sublimed out of the heating zone. The residue in the flask was chromatographed (SiO_2/CH_2Cl_2) to give additional **1** (total yield 0.43 g, 50% based on excess amine) and *N*-1-(ferrocenyl)ethyl-2,3-naphthalimide, **2** (yield 0.30 g, 73% based on the dicarboxylic acid).

Orange-yellow plate-like crystals of **1** sublimed from this oil over an extensive period at ambient temperature. ^{1}H NMR ($CDCl_3$) δ: 6.45 [dd (J = 11, 17 Hz), 1H, –C*H*=CH_2] 5.34 [dd (J = 2, 17 Hz), 1H, –CH=CH_{trans}], 5.03 [dd (J = 2, 11 Hz), 1H, –CH=CH_{cis}], 4.36 (m, 2H, C_5H_4-α) 4.21 (m, 2H, C_5H_4-β), 4.11 (s, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$) δ: 134.7 (–CH=*C*H_2), 111.1 (–*C*H=CH_2), 83.6 (C_5H_4-ipso), 69.3 (C_5H_5), 68.7 (C_5H_4-β), 66.7 (C_5H_4-α).

4. Crystal structure determination

Crystal data for **1** is given in Table 2. An orange-yellow plate-like crystal was mounted on a plastic loop and data were collected at 90(2) K on a Bruker APEXII CCD

Table 1
Selected bond distances (Å) and angles (°) for **1**

C1a–C2a 1.329(4)	C2a–C3 1.494(3)
C1b–C2b 1.320(7)	C2b–C3 1.568(4)
C1a–C2a–C3 119.7(3)	C1b–C2b–C3 115.5(4)