

# Friedel-Crafts acylation of $W(CO)_5$ -complexes of azaferrocenes

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## Abstract

Blocking of the lone pair of electrons on the nitrogen in azaferrocene by co-ordination to the  $W(CO)_5$  moiety enables Friedel-Crafts acylation of this heteroferrocene.  $W(CO)_5$ -complexes of azaferrocene and 2,5-dimethylazaferrocene react with acetyl- and propionyl chloride or acetic anhydride in the presence of aluminium chloride in dichloromethane at r.t. to give  $W(CO)_5$ -complexes of 1'-acylazaferrocenes in 10–50% isolated yields. The low yields presumably result from instability of the products in the reaction medium. The X-ray structure of the complex of 1'-acetylazaferrocene has been determined.

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**Keywords:** Azaferrocene; Tungsten pentacarbonyl; Friedel-Crafts reaction; Acylation

## 1. Introduction

Friedel-Crafts acylation is the reaction of central importance in the chemistry of ferrocene [1]. Used for the first time by Woodward et al. [2] to demonstrate the aromatic character of this metallocene, it opened an entry to acyl and 1,1'-diacylferrocenes, that in turn can be transformed into plethora of ferrocene derivatives by classical functional group transformations. With the discovery of heteroferrocenes containing the group 15 heteroatoms in the place of CH groups in the cyclopentadienyl ligands [3,4] the question arose whether these metallocenes can also be acylated by the Friedel-Crafts way. This is not only a question of fundamental academic importance but also a practical one, because such an acylation, similarly as in the case of ferrocene, would open useful routes to a variety of heteroferrocene derivatives.

It has been found that phosphoferrocene, 1,1'-diphosphoferrocene, arsa- and diarsaferrocene do un-

dergo Friedel-Crafts acylation [4,5]. In contrast to this, attempts to achieve Friedel-Crafts acylation (and other electrophilic substitution reaction) of azaferrocene failed. It is believed to be due to deactivation resulting from the higher electronegativity of nitrogen [6] (similarly as pyridine is less reactive toward electrophiles than benzene) and before all to the possible formation of an inactive complex between the electrophile (or acidic promoter) and the nucleophilic nitrogen atom of azaferrocene. In fact, it is known that azaferrocene is acylated at nitrogen by acid chlorides to give cationic complexes and complex formed from 2,3,4,5-tetramethylazaferrocene was isolated and characterised [7].

We thought that if nucleophilicity of the nitrogen is the main factor hampering the electrophilic substitution of azaferrocene, the *N*-coordination of this metallocene to a properly chosen metal centre, blocking the lone pair of electrons at the nitrogen atom will enable such reactions.

Herein we report that  $W(CO)_5$ -complexes of azaferrocene (**1a**) and 2,5-dimethylazaferrocene (**1b**) [8] do undergo Friedel-Crafts acylation by acyl chlorides or anhydrides and aluminum chloride. This is the first

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example of an electrophilic substitution reaction in the azaferrocene system.

## 2. Results and discussion

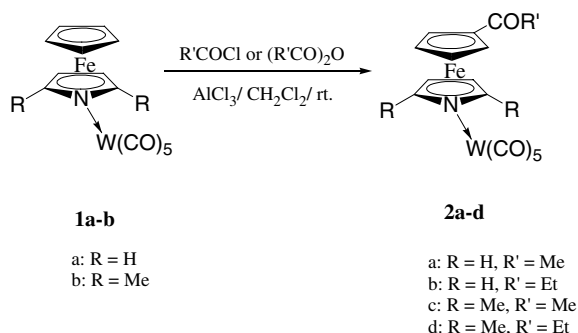
We have found that complexes **1a–b** react with acetyl- and propionyl chloride as well as with acetic and propionic anhydride and aluminum chloride in dichloromethane at r.t. to afford compounds acylated in the Cp ring **2a–d** as the sole isolable products (Scheme 1).

Generally, the complex of 2,5-dimethylazaferrocene **1b** gave highest yields of the acylated products **2c–d** (up to 50%), whereas the complex of azaferrocene **1a** gave only poor (10–20%) yields of **2a–b** along with variable amounts of the recovered starting material. These low yields may result from a gradual decomposition of both **1a–b** and **2a–d** caused by aluminum chloride. The acylation reaction competes with the decomposition.

The substitution in the Cp ring was confirmed by  $^1\text{H}$  NMR spectra of **2a–d**, displaying apart from signals assignable to the R' group and to the protons of the pyrrolyl ligands, two distinct two-proton signals assignable to the substituted Cp ligand. The structure of **2a** was also confirmed by X-ray diffraction. The structure is shown in Fig. 1, crystal and structure refinement data in Table 1 and selected bond lengths and angles in Table 2.

The 1'-acetylaazaferrocene ligand in **2a** adopts a nearly eclipsed conformation (to compare with both eclipsed and staggered conformation of azaferrocene existing in the crystals of its  $\text{W}(\text{CO})_5$ -complex [8]). The acetyl group is practically coplanar with the Cp ring suggesting conjugation between these fragments. Molecular packing of **2a** is shown in Fig. 2. Two intermolecular C–H...O bonds present (not shown in Fig. 2) are described in Table 3.

The selective formation of Cp-substituted products in the above reaction may be explained by both electronic and steric factors. It has been found that azaferrocene coordinates to the  $\text{W}(\text{CO})_5$  moiety acting mainly as a  $\sigma$ -donor [8]. This should bring about a decrease of the



Scheme 1.

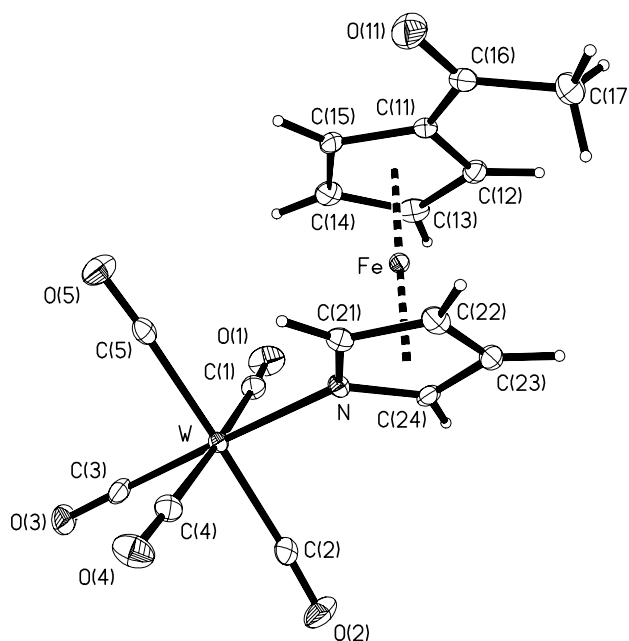


Fig. 1. Molecular structure of **2a**.

electronic density in the pyrrolyl ligand, thereby favoring electrophilic attack on the Cp ring. Such an attack should also be favored by the steric hindrance of the  $\text{W}(\text{CO})_5$  entity, hampering access to the pyrrolyl ligand.

The above results demonstrate that blocking of the lone pair of electrons of nitrogen via coordination to a metal centre enables Friedel-Crafts acylation of the azaferrocene system. In the case of the  $\text{W}(\text{CO})_5$  moiety acylation occurs at the Cp-ring but we believe that by

Table 1  
Crystal data and structure refinement for **2a**

Compound	<b>2a</b>
Chemical formula	$\text{C}_{16}\text{H}_{11}\text{FeNO}_6\text{W}$
Formula weight	552.96
<i>T</i> (K)	100(1)
Space group	$P2_1/c$
Crystal system	Monoclinic
Unit cell dimensions	
<i>a</i> (Å)	10.659(1)
<i>b</i> (Å)	10.863(1)
<i>c</i> (Å)	15.081(1)
$\beta$ (°)	106.88(3)
<i>V</i> (Å <sup>3</sup> )	1671.0(2)
<i>Z</i>	4
Diffraction geometry	$\omega$
Theta range (°)	3.34 to 28.38
Number of reflections measured	10087
Number of unique reflections	3846
$R_{\text{int}}$	0.0243
Number of observed reflections	3421 [ $I > 2\sigma(I)$ ]
Number of parameters	226
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0175$ , $wR_2 = 0.0375$
Final <i>R</i> indices (all data)	$R_1 = 0.0224$ , $wR_2 = 0.0385$
Goodness-of-fit ( <i>S</i> )	1.087

Table 2  
Selected bond lengths (Å) and angles (°) for **2a**

W–C(3)	1.967(3)
W–C(2)	2.035(3)
W–C(4)	2.040(3)
W–C(1)	2.049(3)
W–C(5)	2.054(3)
W–N	2.252(2)
O(11)–C(16)	1.219(3)
O(1)–C(1)	1.137(4)
O(2)–C(2)	1.147(4)
O(3)–C(3)	1.161(3)
O(4)–C(4)	1.144(4)
O(5)–C(5)	1.138(4)
C(11)–C(16)	1.476(4)
C(16)–C(17)	1.503(4)
C(15)–C(11)–C(16)	124.4(2)
C(12)–C(11)–C(16)	127.4(3)
O(11)–C(16)–C(11)	119.6(3)
O(11)–C(16)–C(17)	121.8(3)
C(11)–C(16)–C(17)	118.6(3)
C(15)–C(11)–C(16)–O(11)	–15.4(4)
C(12)–C(11)–C(16)–O(11)	171.7(3)
Fe–C(11)–C(16)–O(11)	–101.8(3)

changing the character of the metal centre it will be possible to tune the reactivity of the co-ordinated azaferrocene and direct electrophilic attack to the pyrrolyl ligand. We hope that the described reaction will contribute to the development of synthetic methods in the chemistry of azaferrocene, which attracted considerable attention in recent years [9]. We are currently looking for metal moieties better compatible with the conditions of the Friedel-Crafts reactions than the  $W(CO)_5$  moiety, strongly activating azaferrocene towards electrophilic

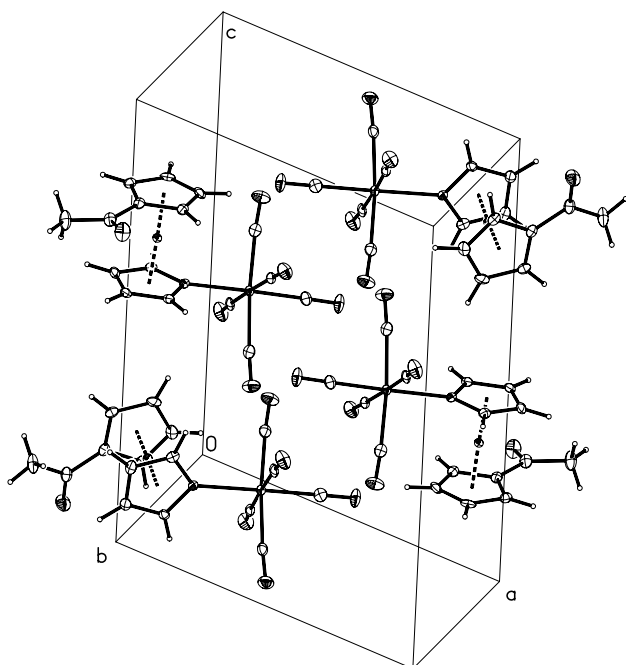


Fig. 2. Crystal packing of **2a**.

Table 3  
Hydrogen bonds in **2a** (Å and °)

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
C(12)–H(12A)···O(3) <sup>a</sup>	0.98	2.36(1)	3.291(2)	158(1)
C(21)–H(21A)···O(11) <sup>b</sup>	0.98	2.25(1)	3.188(2)	160(1)

Symmetry transformations used to generate equivalent atoms.

<sup>a</sup>  $x - 1, y, z$ .

<sup>b</sup>  $-x, -y + 2, -z$ .

attack, and finally, easily removable after the reaction to afford the substituted azaferrocene.

### 3. Experimental

All reactions were carried out under an argon atmosphere. Chromatographic separations were performed using Silica gel 60 (Merck, 230–400 mesh ASTM). The NMR spectra were run on a Varian Gemini 200 BB (200 MHz for  $^1H$ ), IR spectra on a FT-IR Nexus and mass spectra on a Finnigan MAT 95 spectrometer. Compounds **1a** and **1b** were prepared according to the earlier published procedure [8].

General procedure: **1a** or **1b** (0.36 mmol) dissolved in dichloromethane (10 cm<sup>3</sup>) was treated with acyl chloride or anhydride (0.72 mmol) and  $AlCl_3$  (144 mg, 1.1 mmol). The orange coloration of the reaction mixture turned gradually violet. After 1 h stirring at r.t. the reaction mixture was poured onto satd. aqueous  $Na_2CO_3$  and extracted with dichloromethane. Flash chromatography ( $SiO_2$ /dichloromethane) afforded **2a–d**.

Compounds **2a–d** gave correct elemental analyses.

**2a**: Yield: 13% (using acetylchloride).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ ): 5.72 (s, 2H,  $\alpha$ -pyrrolyl), 5.04 (t,  $J = 1.7$  Hz, 2H,  $C_5H_4$ ), 4.87 (t,  $J = 1.7$  Hz, 2H,  $C_5H_4$ ), 4.72 (s, 2H,  $\beta$ -pyrrolyl), 2.49 (s, 3H,  $CH_3$ ). IR ( $CHCl_3$ ,  $\nu$  [ $cm^{-1}$ ]): 1927 (broad,  $C\equiv O$ ), 1682 ( $C=O$ ). MS (EI, 70 eV): 552.9 [ $M^+$ ], 524.9 [ $M - CO^+$ ], 468.9 [ $M - 3CO^+$ ], 229.0 [ $M - W(CO)_5^+$ ].

**2b**: Yield: 10% (using either propionyl chloride or propionic anhydride).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ ): 5.69 (s, 2H,  $\alpha$ -pyrrolyl), 5.05 (t,  $J = 1.8$  Hz, 2H,  $C_5H_4$ ), 4.84 (t,  $J = 1.8$  Hz, 2H,  $C_5H_4$ ), 4.69 (s, 2H,  $\beta$ -pyrrolyl), 2.81 (q,  $J = 7.2$  Hz, 2H,  $CH_2$ ), 1.21 (t,  $J = 7.2$  Hz, 3H,  $CH_3$ ). IR ( $CHCl_3$ ,  $\nu$  [ $cm^{-1}$ ]): 1927 (broad,  $C\equiv O$ ), 1682 ( $C=O$ ). MS (EI, 70 eV): 566.9 [ $M^+$ ], 538.8 [ $M - CO^+$ ], 426.9 [ $M - 5CO^+$ ], 243.0 [ $M - W(CO)_5^+$ ].

**2c**: Yield: 18% (using acetyl chloride), 50% (using acetic anhydride).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ ): 4.83 (t,  $J = 2.0$  Hz, 2H,  $C_5H_4$ ), 4.66 (t,  $J = 2.0$  Hz, 2H,  $C_5H_4$ ), 4.62 (s, 2H,  $\beta$ -pyrrolyl), 2.58 (s, 6H,  $CH_3$ -pyrrolyl), 2.43 (s, 3H,  $CH_3$ ). IR ( $CHCl_3$ ,  $\nu$  [ $cm^{-1}$ ]): 1925 (broad,  $C\equiv O$ ), 1678 ( $C=O$ ). MS (EI, 70 eV): 580.8 [ $M^+$ ], 524.8 [ $M - 2CO^+$ ], 496.8 [ $M - 3CO^+$ ], 257.0 [ $M - W(CO)_5^+$ ].

**2d**: Yield: 20% (using propionyl chloride)  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ ): 4.84 (t,  $J = 1.9$  Hz, 2H,  $C_5H_4$ ), 4.65 (t,

$J = 1.9$  Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 4.60 (s, 2H,  $\beta$ -pyrrolyl), 2.74 (q,  $J = 7.2$  Hz, 2H, CH<sub>2</sub>), 2.57 (s, 6H, CH<sub>3</sub>-pyrrolyl), 1.21 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>). IR (CHCl<sub>3</sub>,  $\nu$  [cm<sup>-1</sup>]): 1925 (broad, C $\equiv$ O), 1680 (C=O). MS (EI, 70eV): 594.8 [M<sup>+</sup>], 566.8 [M - CO<sup>+</sup>], 538.7 [M - 2CO<sup>+</sup>], 510.8 [M - 3CO<sup>+</sup>], 271.0 [M - W(CO)<sub>5</sub><sup>+</sup>].

### 3.1. X-ray structure determination

Crystal data collection and refinement are summarized in Table 1. Preliminary examination and intensities data collections were carried out on a KUMA KM-4  $\kappa$ -axis diffractometer with graphite-monochromated Mo K $\alpha$  and CCD camera. The data were corrected for Lorentz, polarization, absorption effects. Data reduction and analysis were carried out with the Kuma Diffraction programs [10]. The structures were solved by direct methods and refined by the full-matrix least-squares method on all  $F^2$  data using the SHELXTL software [11]. Carbon bonded hydrogen atoms were included in calculated positions and refined in the riding mode. All non-hydrogen atoms were refined with anisotropic displacement parameters. Experimental details, atom's coordinates and displacement parameters are deposited with the Cambridge Crystallographic Data Centre, CCDC 240871. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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