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SHORT COMMUNICATION
IRON DIPROTONATED [1.1] FERROCENOPHANE GENERATED IN SUPER-ACID AND DIRECTLY OBSERVED BY NMR SPECTROSCOPY

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[1.1]Ferrocenophane (1) has been shown to catalyze the photochemical splitting of water and iron diprotonated [1.1]ferrocenophane has been postulated as a reactive intermediate in this process. However, it has previously not been possible to observe the species directly by, e.g., NMR spectroscopy, since under the conditions it rapidly eliminates hydrogen. By employing a special ion generation technique, 1 has been pronated in superacid (FSO_3H–SO_2CIF) at − 125°C. Under these conditions, the cation formed has a long lifetime and its structure and dynamics have been studied by NMR spectroscopy. The ion observed is iron diprotonated [1.1]ferrocenophane (2), which undergoes rapid degenerate rearrangements. $^1H^1H$ NOESY experiments suggest that in 2 the cyclopentadienyl rings in the ferrocene units are tilted relative to each other. © 1997 John Wiley & Sons, Ltd.

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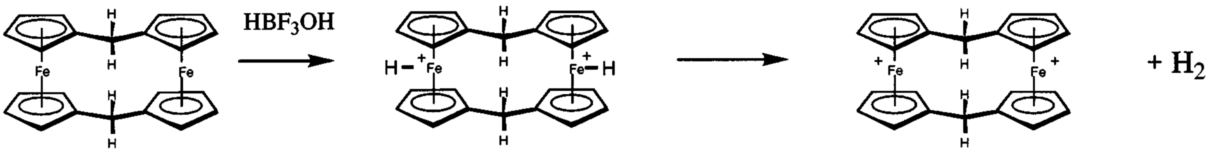
INTRODUCTION

[1.1]Ferrocenophane (**1**) has been shown to dissolve in strong non-oxidizing acids such as trifluoroboric acid (HBF_3OH) to yield immediately hydrogen gas and the dication (**3**). The iron diprotonated species (**2**) has been suggested to be a reactive intermediate in this reaction, but has previously not been directly observed.[1] Compound **2** has also been proposed to be an intermediate in photochemcial splitting of water catalyzed by **1** in solar energy systems.[2]

In this paper, we report the first direct observation of **2** by NMR spectroscopy. By employing a special ion generation technique described previously[3] it has been possible to generate **2** under conditions of long lifetime and to study its structure and dynamics directly by NMR spectroscopy.

RESULTS AND DISCUSSION

A degassed dideuteromethylene chloride (CD_2Cl_2) solution of a few milligrams of **1** was mixed at − 125°C into a degassed mixture of FSO_3H and SO_2C1F (1:10) (superacid). Upon mixing, the solution instantaneously turned blue–green. The ^1H NMR spectrum of the solution was obtained at − 122°C with a Varian Unity 500 instrument operating at



1 **2** **3**

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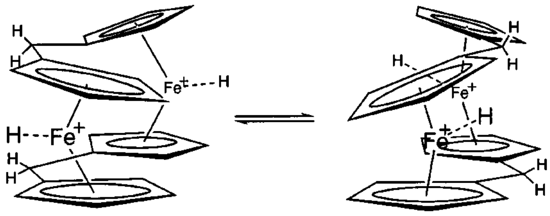
499·92 MHz. The spectrum in Figure 1 shows four different singlets at δ1·21, 3·54, 4·77 and 5·55 ppm with the relative intensities 2:4:8:8.

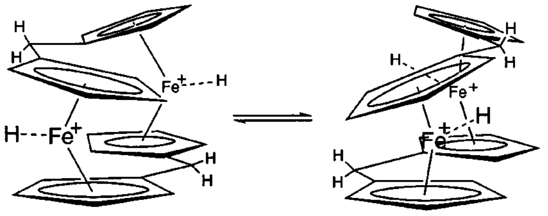
The small number of signals indicate that the ion is not a static ion but is rather undergoing fast (on the NMR time-scale) degenerate rearrangements. The signal at δ-1·21 ppm is ascribed to two protons bonded to iron(s). These protons are likely bonded to different irons and the protons may or may not exchange rapidly with each other. However, our present knowledge does not exclude the possibility that both protons are bonded to the same iron. If this is the case, the protons are rapidly transferred between the irons.



2a **2a**

Ion **2** may have a *syn* structure (**2a**) (or rather a twisted *syn* structure) undergoing a fast degenerate rearrangement (pseudorotation[4]) and with, e.g., the protons located as indicated.

The results obtained so far do not exclude the possibility that ion **2** has an *anti* structure[5] (**2b**) (or rather a twisted *anti* structure) undergoing a rapid identity reaction as shown.



2b **2b**

The assignment of the ^{1}H NMR resonances were made based on ^{1}H,^{1}H NOESY results obtained at −122°C that are given in Table 1.

Through the degenerate rearrangements the α'-protons exchange with the α'' protons and the β'-protons with the β''-protons. Thus the α'/α'' and β'/β'' protons appear at δ 4·77 and 5·55, respectively, and the methylene bridge protons resonate at δ 3·54. The strong NOE on the FeH proton from the α'/α'' protons compared with that from the β'/β'' protons and the presence of the weak NOE from the methylene protons indicate that the FeH protons are on the average closer to the α'/α'' protons than to the β'/β'' protons. This suggests that **2** may have a structure with

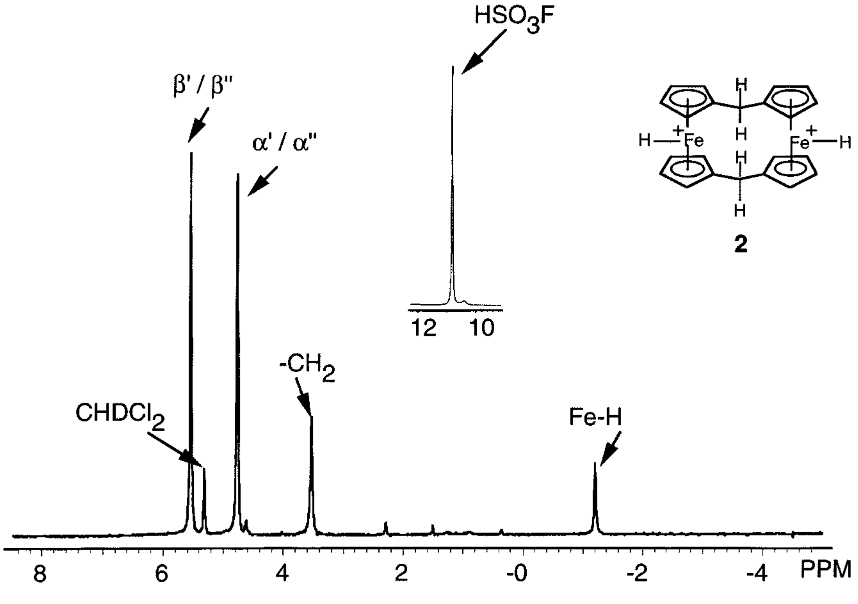


Figure 1. ^{1}H NMR spectrum of **2** at −122°C in $FSO_3H–SO_2ClF$ (1:10)

Tables 1. Chemical shifts and NOEs for the protons in the iron diprotonated ferrocenophane **2** obtained at -122°C.

Proton #	δ/ppm[a]	Protons and associated NOEs[b]
β'/β''	5·.55	α'/α''*s*, Fe-H
α'/α''	4·77	β'/β''*s*, CH_2, Fe-H*s*
CH_2	3·54	α'/α''*s*, β'/β''*w*, Fe-H
Fe-H	$-1{\cdot}21$	α'/α''*s*, β'/β'', CH_2 *w*

[a] The proton chemical shifts (δ) are referenced to $CHDCl_2$ $\delta = 5{\cdot}32$

[b] Weak and strong NOEs are indicated by *w* and *s* respectively.

tilted cyclopentadienyl rings.

The ^1H decoupled ^{13}C NMR spectrum shows only four signals from ion **2**. These signals appear at δ 101·28, 82·22, 75·06 and 24·26 ppm with relative intensities 4:8:8:2 and are ascribed to the methine, ring and methylene bridge carbons, respectively. It has not been possible to assign the β'/β'' and α'/α'' ring carbons.

When the temperature is raised to -80°C, ion **2** decomposes to unidentified products. At the present stage it is not known whether this takes place via elimination of hydrogen or by some other route.

ACKNOWLEDGMENTS

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