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Synthesis and reactivity of a new Fe(II) 5-(4-pyridyl)-tetrazolate complex and X-ray structure of its doubly protonated derivative.

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Abstract

The synthesis of the new Fe(II) complex [$CpFe(CO)_2(N_4C{-}C_5H_4N)$] (**2**) is described. ^1H- and ^{13}C-NMR spectroscopy data of (**2**) indicate the presence of interannular conjugation in the pyridyl-tetrazolate ligand, implying coplanarity between the two rings. Addition of electrophiles to **2** resulted in the formation of cationic complexes such as [$CpFe(CO)_2(4\text{-}MeN_4C{-}C_5H_4N)$][$O_3SCF_3$] (**3**), [$CpFe(CO)_2(4\text{-}HN_4C{-}C_5H_4N)$][$O_3SCF_3$] (**4**) and of the doubly protonated complex [$CpFe(CO)_2(4\text{-}HN_4C{-}C_5H_4N{-}H)$][$O_3SCF_3$]$_2$ (**5**). In all cases, the out-of-plane rotation of the pyridyl ring occurred as a consequence of the quaternization of the N-4 of tetrazole ring. X-ray structure of complex **5** indicates a torsion angle of 20.9(2)° between the aromatic rings. Protonation reactions were found to be reversible and complexes **4**–**5** were easily converted into the starting complex **2** by addition of a base.

Keywords: Fe(II) organometallic complexes; Interannular conjugation; Tetrazolate ligands; X-ray diffractometry

1. Introduction

In the last two decades tetrazole derivatives, owing to their peculiar properties, have been extensively studied. Indeed, the tetrazolic acid group $-CN_4H$ shows similar acidity and higher metabolic stability than the carboxylic acid group. These features have favoured the replacement of $-CO_2H$ group by the isosteric $-CN_4H$ moiety in several biologically active molecules, prompting the rapid development of tetrazole-based compounds in several areas of research connected to medicinal science [1]. A typical synthetic pathway leading to tetrazole systems is given by the [2+3] cycloaddition reaction between organonitriles and azido salts or miscellaneous (silyl, stannyl, aliphatic or aromatic) azido derivatives [2,3]. Since the early work by Beck and co-workers [4,5], it has been demonstrated that the presence of metal ions in such reactions allows the cycloaddition to run in mild conditions and good yields. In particular, the synthesis of a metal bound tetrazole ring can be easily achieved either by addition of organonitriles to azido complexes [6], or by reaction of azide salts with an appropriate metal-coordinated nitrile [7]. As a further example of the latter procedure, we have recently prepared new organometallic Fe(II) 5-aryl tetrazolate complexes such as [$CpFe(CO)(L)(N_4C{-}C_6H_4{-}CN)$], [L = CO; PPh_3; $P(OCH_3)_3$; CN-2,6-$Me_2C_6H_3$] under mild conditions by addition of sodium azide to the parent 1,4 dicyanobenzene complexes [8]. The characterisation of the produced complexes allowed us to establish some interesting features such as the regioselective formation of N-2 coordinated isomers and a not significant interannular conjugation effect in the 5-aryl tetrazolate ligand, involving the coplanarity between tetrazole and phenyl rings. Reactions of Fe(II) 5-aryl tetrazolate complexes with electrophiles such as CH_3^+ or H^+ resulted in the regioselective quaternization of the N-4 of the tetrazole ring causing, in all cases, the out-of-plane rotation of the phenyl ring and the consequent reduction of interannular conjugation. Noteworthy in the reversibility of the protonation reaction

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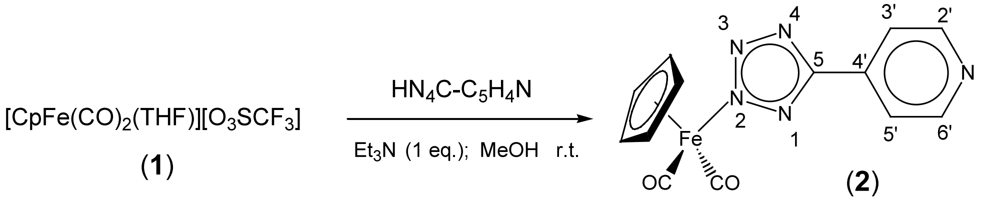
which introduces the possibility of modulating the conjugative properties of the 5-aryl tetrazolate ligand by an acid–base mechanism. In order to further substantiate our results, we now report the synthesis of a new Fe(II) organometallic complex bearing 5-(4-pyridyl)-tetrazolate ligand and the X-ray structure of its doubly protonated derivative.

2. Results and discussion

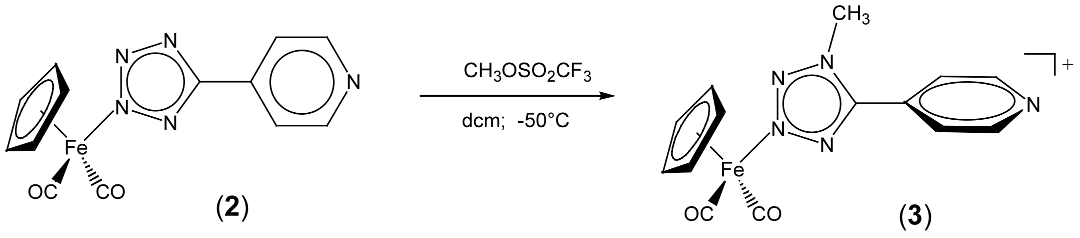
2.1. General

The synthetic approach used in this study to prepare pure and well defined target complexes is outlined in Eq. (1).



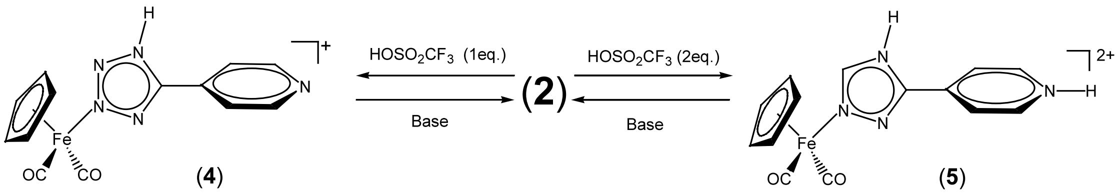
(1)

The precursor complex $[CpFe(CO)_2(THF)][O_3SCF_3]$ (**1**) was prepared from the corresponding iodide [9] by reaction with a slight excess (1.1 equivalent) of silver triflate in THF (15 ml) at room temperature for 4 h. Filtration through a Celite pad and subsequent evaporation to dryness afforded a deep red solid which was used without any further purification. The preparation of the 5-(4-pyridyl)-tetrazolate anion was easily achieved by adding a stoichiometric amount of triethylamine to a suspension in methanol (5 ml) of 4-(*1H*-tetrazol-5-yl)-pyridine, which was prepared in 82% yield from 4-cyanopyridine by following a literature procedure [10]. Therefore, starting reagents were mixed in methanol at room temperature to afford the complex $[CpFe(CO)_2\text{-}(N_4C\text{–}C_5H_4N)]$ (**2**) in 45% yield, this value being affected by the presence of the undesired dimeric species $[Fe_2Cp_2(CO)_4]$, to the formation of which could not be avoided even though the metathesis reaction was performed at low temperature. Methylated (**3**) (Eq. (2)) and protonated complexes (**4** and **5**) (Scheme 1) were obtained by addition of appropriate amounts of methyl triflate or triflic acid, respectively.



(2)

The main FT-IR and NMR (^1H, ^{13}C) spectroscopic data of all compounds are summarized in Table 1.



Scheme 1.

Table 1
NMR (^{1}H, ^{13}C) [a] and FT-IR [b] data for complexes **2**–**5**

Entry	δC_5 (ppm)	$\delta H_{2',6'}$ (ppm)	$\delta H_{3',5'}$ (ppm)	$\delta C_{2',6'}$ (ppm)	$\delta C_{3',5'}$ (ppm)	CO absorption (cm^{-1})
2	164.2	8.69	7.94	150.4	120.1	2066; 2020
3	154.1	8.90	8.34	147.5	128.5	2074; 2029
4	156.7	8.87	8.51	143.7	125.2	2068; 2024
5	153.9	8.98	8.56	143.9	125.1	2075; 2030

[a] CD_3CN as solvent.
[b] CH_2Cl_2 as solvent.

2.2. IR spectroscopy

As expected, the formation of the neutral complex [$CpFe(CO)_2(N_4C-C_5H_4N)$] (**2**) was witnessed by the shift of the carbonyl bands of the cationic precursor **1** [IR(CH_2Cl_2) 2074; 2030 cm^{-1}] to lower wave numbers [IR(CH_2Cl_2) 2066; 2020 cm^{-1} for **2**]. These values are coincident with those reported for [$CpFe(CO)_2(N_4C-C_6H_4-CN)$] [8], but higher than those in [$CpFe(CO)_2(CN)$] [IR(CH_2Cl_2) 2054; 2014 cm^{-1}] and comparable to the ones in [$CpFe(CO)_2(CNW(CO)_5)$] [IR(CH_2Cl_2) 2064; 2024 cm^{-1}] [11]. This fact could indicate the presence of a back-bonding interaction to the tetrazolate ring in complex **2**. Addition of electrophiles resulted in the shift of the carbonyl absorptions to higher frequency both for the methylated complex (**3**) [IR(CH_2Cl_2) 2074; 2029 cm^{-1}] and for the protonated derivatives **4** [IR(CH_2Cl_2) 2068; 2024 cm^{-1}] and **5** [IR(CH_2Cl_2) 2075; 2030 cm^{-1}].

2.3. NMR study

As mentioned in the Introduction section. We recently prepared [8] some new 5-aryl tetrazolate Fe(II) organometallic complexes. Due to the presence of two non-equivalent nitrogen atoms in the tetrazole ring, the first goal in the characterization of such compounds consisted in the determination of the binding site of the metal fragment to the tetrazolate ligand. To do this, we took into account some NMR studies reported by Butler [12], in which the chemical shift of C_5 tetrazole has been used as a probe to distinguish between N-1 ($\delta C_5 = 152-157$ ppm) and N-2 methylated ($\delta C_5 = 162-167$ ppm) derivatives of a series of 5-aryl tetrazoles. In all the 5-aryl tetrazolate complexes we prepared, the ^{13}C chemical shift values of the tetrazole carbon ($\delta C_5 = 164-165$ ppm) indicated the regiospecific coordination at N-2 of tetrazole ring. The X-ray structure of the complex [$CpFe(CO)(P(OMe)_3)(N_4C-C_6H_4-CN)$] evidenced both the coordination at N-2 of the organometallic fragment and the coplanarity between the tetrazole and aryl rings. Likewise, in the present work complex [$CpFe(CO)_2(N_4C-C_5H_4N)$] (**2**) exhibits the chemical shift of C-5 at 164.2 ppm, suggesting the exclusive coordination of the metal fragment at N-2 of the tetrazole ring (Eq. (1)). It has been established that coplanarity between the aromatic rings in organic N-2 substituted 5-aryl tetrazoles [13] as well as in the corresponding N-2 coordinated metal complexes [14,15] implies interannular conjugation, which is absent in the parent N-1 derivatives. As we reported [8], interannular conjugation in 5-aryl tetrazolate complexes is removed, or strongly diminished, when a substituent at N-4 of tetrazole ring induces rotation about the tetrazole-aryl bond away from coplanarity. In particular, the out of plane rotation of the aryl ring resulted in the downfield shift of the carbons *ortho* to the tetrazole group. In light of those results, we performed electrophilic additions to complex **2**, which was at first converted into the methylated cationic product **3** by treatment with one equivalent of methyl triflate. The methylation reaction occurs selectively at the position **4** of tetrazole ring (Eq. (2)), as evidenced by the ^{13}C chemical shift of C-5 at 154.1 ppm, which is typical of tetrazoles having a substituent on the nitrogen adjacent to the tetrazole carbon [16,17]. Interestingly, we did not have any evidence of the presence of methyl group bonded to the pyridine nitrogen, whereas such selectivity was not reported for the electrophilic attack onto 4-(*1H*-tetrazol-5-yl)-pyridine [18]. This behaviour could indicate an increased electron density on the metal-coordinated tetrazole ring with respect to the free ligand, providing a further evidence of a metal-to-ligand electron donating interaction, whose presence was previously detected by IR spectroscopy. Moreover, a noticeable downfield shift of pyridine C-3′ and C-5′

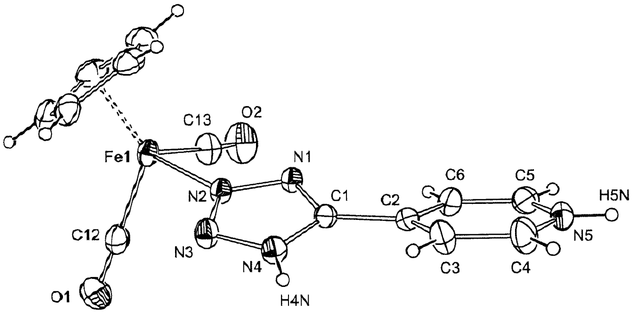


Fig. 1. An ORTEP plot of the molecular structure of [$CpFe(CO)_2(HN_4C-C_5H_4N-H)$]$^{2+}$ (**5**). Thermal ellipsoids are drawn at the 30% probability level.

Table 2
Selected bond lengths (Å) and bond angles (°) for **5**

Bond lengths			
Fe(1)–N(2)	1.956(2)	N(4)–C(1)	1.332(4)
Fe(1)–C(12)	1.793(4)	C(1)–C(2)	1.469(4)
Fe(1)–C(13)	1.791(4)	C(2)–C(3)	1.379(5)
C(12)–O(1)	1.139(5)	C(3)–C(4)	1.375(5)
C(13)–O(2)	1.124(5)	C(5)–C(6)	1.365(5)
N(1)–N(2)	1.340(4)	C(6)–C(2)	1.378(5)
N(2)–N(3)	1.303(4)	N(5)–C(4)	1.325(5)
N(3)–N(4)	1.327(4)	N(5)–C(5)	1.328(5)
N(1)–C(1)	1.316(4)		
Bond angles			
C(12)–Fe(1)–N(2)	92.4(1)	C(12)–Fe(1)–C(13)	95.2(2)
C(13)–Fe(1)–N(2)	92.6(1)		
Interplanar angle			
C(tetrazole)–C(pyridyl)	20.9(2)		

was observed in going from complex **2** ($\delta C_{3',5'} = 120.1$ ppm) to the corresponding cationic compound **3** ($\delta C_{3',5'} = 128.5$ ppm). The analysis of such NMR data led us to assume the presence of some interannular conjugation effect in complex **2**, that is removed or strongly reduced in complex **3**, in which the presence of a methyl group bonded at the nitrogen adjacent to the tetrazole carbon results in the out-of-plane rotation of the pyridyl ring. Reaction of complex **2** with one equivalent of triflic acid (see Scheme 1) afforded the protonated complex **4**, in which the preferential protonation at N-4 of tetrazole ring is shown by δC_5 at 156.7 ppm and the diminution of interannular conjugation effect is indicated by the variation of chemical shift of C-3′ and C-5′ ($\delta C_{3',5'} = 125.2$ ppm versus 120.1 ppm in **2**). At the same time, it turns out that the reduced steric hindrance of the hydrogen substituent with respect to the methyl group results in a lower downfield shift of $\delta C_{3',5'}$. Protonation of complex **2** was also carried out with two equivalents of triflic acid in order to neutralize the basic properties of the pyridine nitrogen. The NMR values of the obtained diprotonated derivative **5** slightly differed from the monocation **4** while a significant difference between them was evidenced by their IR spectra (see Table 1). The reversibility of such reactions was evidenced by addition of the proper amount (one or two equivalents) of triethylamine to complexes **4** and **5**, causing in both cases the quantitative reformation of the neutral precursor **2**.

Table 3
Crystal data and experimental details for **5**

Formula	$C_{15}H_{11}F_6FeN_5O_8S_2$
M	623.26
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	15.3345(7)
b (Å)	8.3672(4)
c (Å)	18.725(1)
β (°)	103.789(2)
V (Å^3)	2333.3(2)
Z	4
D_{calc} (Mg m^{-3})	1.774
Absorption coefficient (mm^{-1})	0.926
F(000)	1248
Crystal size (mm^3)	0.40 × 0.35 × 0.30
θ limits (°)	2.68–28.00
Reflections collected	23411 ($\pm h$, $\pm k$, $\pm l$)
Unique observed reflections [$F_o > 4\sigma(F_o)$]	5580
Goodness-of-fit on F^2	1.004
Final $R_1(F)$ [$I > 2\sigma(I)$]	0.0565
$wR_2(F^2)$ (all data)	0. 1613
Largest difference peak and hole (e Å^{-3})	0.818 and −0.713

2.4. X-ray discussion

The molecular structure of the dication **5** is shown in Fig. 1 and its stereogeometry is that expected on the basis of the spectroscopic evidence.

Bond distances of interest are listed in Table 2. A comment is worth for Fe–N(tetrazole) 1.956(2) Å and C(tetrazole)–C(pyridine) 1.469(4) Å. These values are equal, within experimental errors, to those recently reported in the similar molecule $[CpFe(CO)\{P(OMe)_3\}(N_4C{-}C_6H_4{-}CN)]$ [8], [1.950(2) and 1.463(3) Å, respectively]; the only difference between the two five-substituted tetrazole ligands being the inter-ring angle 3.3(2)° for $N_4C{-}C_6H_4{-}CN$ and 20.9(2)° for $HN_4C{-}C_5H_4N{-}H$. The latter value confirms the previously discussed independence of the C(tetrazole)–C(phenyl) on the inter-ring angle, i.e. the inter-ring conjugation of the π orbitals is small and not detectable in terms of bond distances (Table 2).

3. Conclusions

The reaction of the cationic complex (**1**) with the pyridyl–tetrazolate anion $[N_4C{-}C_5H_4N]^-$ led to the new organometallic complex $[CpFe(CO)_2(N_4C{-}C_5H_4N)]$ (**2**). The NMR spectroscopic characterization of **2** indicated both the regioselective coordination of the organometallic fragment at N-2 of tetrazole ring and the presence of interannular conjugation effect in the pyridyl tetrazolate ligand, involving coplanarity between the two rings. These latter properties were modified by addition of electrophilic species, which resulted in the formation of N-4 alkylated derivative such as $[CpFe(CO)_2(4\text{-}MeN_4C{-}C_5H_4N)][O_3SCF_3]$ (**3**) or N-4 protonated complexes such as $[CpFe(CO)_2(4\text{-}HN_4C{-}C_5H_4N)][O_3SCF_3]$ (**4**) and $[CpFe(CO)_2(4\text{-}HN_4C{-}C_5H_4N{-}H)][O_3SCF_3]_2$ (**5**). The X-ray structure of complex **5** confirmed the presence of a torsion angle of 20.9(2)°

between the aromatic rings. At the same time, no particular distortion of the pyridyl tetrazolate inter-ring distance, consequent to diminution of conjugative properties, was observed. However, since protonation reactions were found to be reversible, it could be possible to modify the structural and electronic features of the target complex **2** by a proton addition-elimination mechanism. Finally, it is worth noting that the complexes **2**–**5** might represent good models for studying the properties of differently substituted tetrazoles, whereas the parent organic systems are normally obtained less selectively or using more drastic conditions [19].

4. Experimental

4.1. General considerations

All reactions with organometallic reagents or substrates were carried out under argon using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. Unless otherwise stated, chemicals were obtained commercially (e.g. Aldrich) and used without any further purification. All the obtained products were characterised by elemental analysis and spectroscopic methods. IR spectra were recorded with a FT-IR spectrometer Perkin Elmer spectrum 2000. The routine NMR spectra (^{1}H, ^{13}C) were always recorded using a Varian Gemini 300 instrument (^{1}H, 300.1; ^{13}C, 75.5 MHz). The spectra were referenced internally to residual solvent resonance, and were recorded at 298 K for characterisation purposes. Elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. Petroleum ether (Etp) refers to a fraction of b.p. 60–80 °C. Typically, all chromatographies were performed on alumina filled column (diameter: 1.5 cm; height 15 cm) under an Argon atmosphere and using dichloromethane–acetonitrile mixtures as eluant.

4.2. Synthesis of *[CpFe(CO)$_2$(N$_4$CC$_5$H$_4$N)]* (**2**)

Complex **1** (0.500 g; 1.26 mmol), dissolved in methanol (5 ml), was added dropwise to a solution of 4-(*1H*-tetrazol-5-yl)-pyridine (0.185 g, 1.26 mmol) and triethylamine (0.18 ml; 1.30 mmol) in methanol (15 ml). The resulting yellow–brown suspension was stirred at room temperature for 6 h., during which time the disappearance of cationic species was monitored by IR spectroscopy. Filtration through a Celite pad and evaporation to dryness afforded a reddish-brown crude product which was purified by alumina filled column. After a first red fraction of [Fe$_2$Cp$_2$(CO)$_4$], the target complex **2** (0.183 g, 45%) was recovered as a yellow microcristalline powder by eluting with a dichloromethane–acetonitrile 5:1 mixture. NMR: δ_H(CD$_3$CN): 8.69 (d, 2H, 2′,6′-C$_5$*H*$_4$N, $^3J_{HH} = 5$ Hz), 7.94 (d, 2H, 3′,5′-C$_5$*H*$_4$N, $^3J_{HH} = 5$ Hz), 5.41 (s, 5H, Cp), δ_C(CD$_3$CN): 210.5 (CO), 164.2 (C-5), 150.4 (2′,6′-*C*$_5$H$_4$N), 136.8 (C-4′), 120.1 (3′,5′-*C*$_5$H$_4$N), 85.8 (Cp); IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2066s (CO), 2020s (CO), 1610w (C=N); Anal. Calc. for C$_{13}$H$_9$N$_5$O$_2$Fe: C, 48.3; H, 2.81; N, 21.7. Found: C, 48.2; H, 2.79; N, 21.5%.

4.3. Methylation reaction: synthesis of *[CpFe(CO)$_2$(4-MeN$_4$C–C$_5$H$_4$N)][O$_3$SCF$_3$]* (**3**)

A solution of **2** (0.500 g, 0.92 mmol) in CH$_2$Cl$_2$ (20 ml) was treated with CH$_3$OSO$_2$CF$_3$ (0.1 ml, 0.92 mmol) with stirring, at −50 °C for 30 min. The mixture was then allowed to warm to r.t. and stirred for additional 3 h. Evaporation of solvent and chromatography of the brown residue on a short alumina filled column with CH$_2$Cl$_2$ as solvent afforded a first red fraction of [Fe$_2$Cp$_2$(CO)$_4$] that was discharged. Elution with a mixture CH$_2$Cl$_2$–CH$_3$CN (2:1, v/v) gave the complex **3** (0.200 g, 70%), obtained as a pale brown oil. NMR: δ_H(CD$_3$CN): 8.90 (d, 2H, 2′,6′-C$_5$*H*$_4$N, $^3J_{HH} = 7$ Hz), 8.34 (d, 2H, 3′,5′-C$_5$*H*$_4$N, $^3J_{HH} = 7$ Hz), 5.45 (s, 5H, Cp), 4.18 (3H, s, CH$_3$); δ_C(CD$_3$CN): 210.0 (CO), 154.1 (C-5), 147.5 (2′,6′-*C*$_5$H$_4$N), 138.0 (C-4′), 128.5 (3′,5′-*C*$_5$H$_4$N), 87.8 (Cp), 37.6 (CH$_3$); IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2074s (CO), 2029s (CO), 1610w (C=N). Anal. Calc. for C$_{15}$H$_{12}$N$_5$O$_5$FeF$_3$S: C, 37.0; H, 2.48; N, 14.4. Found: C, 36.9; H, 2.45; N, 14.5%.

4.4. Protonation reactions: synthesis of *[CpFe(CO)$_2$(4-HN$_4$C–C$_5$H$_4$N)][O$_3$SCF$_3$]* (**4**) and of *[CpFe(CO)$_2$(4-HN$_4$C–C$_5$H$_4$N–H)][O$_3$SCF$_3$]$_2$* (**5**)

To a stirred solution of **2** (0.300 g, 1.55 mmol) in CH$_2$Cl$_2$ (20 ml), HOSO$_2$CF$_3$ (0.15 ml, 1.55 mmol, diluted in 5 ml of CH$_2$Cl$_2$) was added dropwise at −60 °C. After 30 min the mixture was allowed to warm to r.t. and the solvent removed in vacuo. The resulting mixture was dissolved in 5 ml of acetonitrile and layered with diethyl ether, causing the formation of a yellow microcristalline powder which was identified as the complex **4** (0.65 g, 90%). NMR: δ_H(CD$_3$CN): 8.87 (d, 2H, 2′,6′-C$_5$*H*$_4$N, $^3J_{HH} = 5$ Hz), 8.51 (d, 2H, 3′,5′-C$_5$*H*$_4$N, $^3J_{HH} = 5$ Hz), 5.40 (s, 5H, Cp); δ_C(CD$_3$CN): 210.5 (CO), 156.7 (C-5′), 143.7 (2′,6′-*C*$_5$H$_4$N), 141.2 (C-4′), 125.2 (3′,5′-*C*$_5$H$_4$N), 87.5 (Cp); IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2068s (CO), 2024 s (CO), 1640w (C=N) Anal. Calc. for C$_{14}$H$_{10}$N$_5$O$_5$FeF$_3$S: C, 35.5; H, 2.11; N, 14.8. Found: C, 35.4; H, 2.12; N, 14.9%. Complex **5** (0.77 g, 80%) was obtained in the same manner as **4** by using two equivalents of triflic acid and it was re-crystallised, in the presence of one of two more drops of acid, from an acetonitrile solution layered with petroleum ether at r.t., affording dark yellow plates. NMR: δ_H(CD$_3$CN): 8.98 (d, 2H, 2′,6′-C$_5$*H*$_4$N, $^3J_{HH} = 9$ Hz), 8.56 (d, 2H, 3′,5′-C$_5$*H*$_4$N, $^3J_{HH} = 9$ Hz), 5.46 (s, 5H, Cp); δ_C(CD$_3$CN):

209.7 (CO), 153.9 (C-5′), 143.9 (2′,6′-C_5H_4N), 138.3 (C-4′), 125.1 (3′,5′-C_5H_4N), 87.0 (Cp); IR (CH_2Cl_2) ν_{max} (cm^{-1}): 2075s (CO), 2030 s (CO), 1647w (C=N). Anal. Calc. for $C_{15}H_{11}N_5O_8FeF_6S_2$: C, 28.9; H, 1.78; N, 11.2. Found: C, 29.1; H, 1.80; N, 11.4%. Addition of one or two equivalents of triethylamine to an acetonitrile solution of complexes **4** or **5**, respectively, reforms quantitatively the neutral precursor **2**.

4.5. X-ray crystallography

A suitable crystal of compound **5** was mounted on a glass fiber in air on a Bruker-AXS SMART CCD area detector diffractometer, using Mo–K_α radiation ($\lambda = 0.71073$ Å) at room temperature. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in three sets of 20 exposures collected in three different ω regions and eventually refined against all reflections. A full sphere of the diffraction space was measured by 0.3° ω steps, 20 s exposures and sample-detector distance kept at 5.0 cm. Intensity decay was monitored by recollecting the initial 50 frames at the end of the data collection and analysing the duplicate reflections. The collected frames were processed for integration by using the program SAINT and an empirical absorption correction was applied using SADABS [20] on the basis of the Laue symmetry of the reciprocal space. The structure was solved by direct methods (SIR-97) [21] and subsequent Fourier syntheses, and refined by full-matrix least-squares calculations on F^2 (SHELXTL) [22] using anisotropic thermal parameters for all non hydrogen atoms. The carbon atoms of the Cp group were found disordered over two sites and an occupancy factor of 0.51(3) was refined for the main image. All hydrogen atoms were located experimentally, but their positions were idealized [$C(sp^2)–H = 0.93$ Å, $N–H = 0.86$ Å] and refined riding the pertinent carbon or nitrogen atoms with isotropic thermal parameters, $U(H) = 1.2U_{eq}$ (C or N). One of the two $[O_3SCF_3]^-$ anions was found disordered (main image with occupancy factor 0.72(1) for the fluorine atoms and occupancy factor 0.86(1) for the oxygen atoms).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 199639 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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