PROTONATION OF THE SULFONAMIDO LIGANDS IN THEIR $Fe(CO)_2Cp$ COMPLEXES

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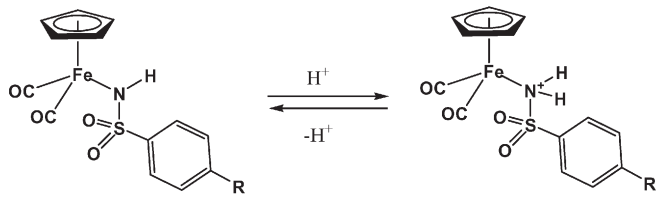
Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contribution to the area of organometallic synthesis and catalysis.

$[Fe(CO)_2Cp(4\text{-}RC_6H_4SO_2NH)]$ complexes (R = Me, NO_2) undergo reversible protonation at the nitrogen atom bonded to the iron centre. The molecular structure of the methyl complex was determined by single crystal X-ray diffraction.

Keywords: Cyclopentadienyl ligands; Iron carbonyl complexes; Sulfonamides; Protonation; X-ray diffraction; Basicity.

The $[Fe(CO)_2Cp]^+$ group (Fp^+) forms with amines (L) cationic complexes $Fp(L)^+$ and with anionic nitrogen ligands L^- (anions of azoles, imides, sulfonamides, barbiturates etc.) neutral complexes FpL [1,2]. Some of the complexes have found applications in bioorganometallic chemistry as IR-detectable protein labelling reagents and haptens in carbonylmetalloimmunoassays or enzyme inhibitors[3]. Neutral complexes FpL contain a three-valent nitrogen atom bearing lone pair of electrons which should endow them with basic properties. Herein we report that neutral Fp complexes with sulfonamido ligands **1a**, **1b** undergo protonation at the nitrogen atom to form cationic Fp(sulfonamide)$^+$ species **2a**, **2b** (Scheme 1).



1a-b **2a-b**

a) R = Me, b) R = NO_2

SCHEME 1

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RESULTS AND DISCUSSION

Addition of $HBF_4 \cdot Et_2O$ to benzene solutions of **1a**, **1b** brings about instantaneous precipitation of orange crystalline water-soluble solids. The treatment of aqueous solutions of these products with potassium carbonate leads to precipitation of the starting complexes **1a**, **1b**.

This means that the **1a**, **1b** are reversibly protonated by HBF_4. The spectroscopic data presented below reveal that protonation takes place at the nitrogen atom and yields the cationic complexes **2a**, **2b**. The IR spectrum of **2a** (Table I) shows two absorption bands in the region of N–H stretching vibrations attributable to the antisymmetric and symmetric vibrations of the NH_2 group (accordingly, complex **1a** shows in this region only one absorption band). Further evidence for the *N*-protonation of **1a**, **1b** was provided by ^{15}N NMR spectra of compounds **1a** and **2a** labelled with ^{15}N. In the spectrum measured without proton decoupling [^{15}N]-**1a** displays a doublet at δ 397 ppm (upfield from the [^{15}N]-nitromethane signal, $J_{15N\text{-}H}$ = 73 Hz), whereas [^{15}N]-**2a** a triplet at δ 337 ppm ($J_{15N\text{-}H}$ = 80 Hz), confirming the presence of one and two hydrogens bonded to nitrogen, respectively. The observed downfield shift (60 ppm) due to the protonation of **1a** is comparable with that observed on protonation of the [^{15}N]-phthalimide anion (74 ppm, chemical shifts of the anion and phthalimide being 302 and 228 ppm, respectively)[4].

Closely similar ^1H NMR and IR data were obtained for **2b** (see Experimental) indicating that protonation of **1b** also occurs at the metal-bound nitrogen atom. The ^1H NMR spectra showed that solutions of **2a** in acetone-d_6 are relatively stable whilst in solutions of **2b** in the same solvent a slow substitution of the 4-nitrobenzene-1-sulfonamide ligand by the solvent took place. It is accompanied by appearance of doublets of aromatic protons at δ 8.43 (J = 9.4 Hz) and 8.17 (J = 9.4 Hz) (**2a** itself shows doublets at δ 8.48 and 8.21 ppm) and of the new Cp signal at δ 5.70 ppm (cf. the corresponding signal of **2b**, 5.62 ppm). The substitution was complete within 24 h. 4-Nitrobenzene-1-sulfonamide was isolated from such a solution and identified by comparison with an authentic sample. We were unable to isolate the iron complex formed (presumably $[Fp(acetone)]^+$) but when halide anions (X^- = Cl^-, Br^- or I^-) were present in the solution, the corresponding halides FpX were isolated. These data indicate that the 4-nitrobenzene-1-sulfonamide ligand can be readily substituted by other 2e donor ligands. In contrast, no reaction of **1b** with halide ligands was observed under the same conditions. This means that the neutral sulfonamide ligand is more substitution-labile that its corresponding anion.

The N–H acidities of **2a**, **2b** were determined by measurement of pH of aqueous solutions of these compounds at known concentration. The pK_a values are 2.9 and 2.7 for **2a** and **2b**, respectively. Therefore, coordination of the Fp^+ moiety to benzenesulfonamide and 4-nitrobenzenesulfonamide (pK_a 9.41 and 8.63, respectively)[5] leads to an important increase (~6–7 pK_a units) of their N–H acidities.

The IR and ^{1}H NMR spectral data of complexes **1a** and **1b** along with the pertinent data measured for 4-methylbenzene-1-sulfonamide are collected in Table I.

It is obvious that frequencies of asymmetric and symmetric stretching vibrations of the SO_2 fragment and the chemical shifts of aromatic, methyl and NH protons decrease in the order: **2a** > 4-methylbenzene-1-sulfonamide > **1a**. This can be rationalized assuming that the coordination of the Fp^+ to the sulfonamide brings about a decrease in the electron density at this ligand, whereas substitution of one of the amido hydrogens with this group causes an opposite effect due to repulsion between iron d electrons and the lone pair of electrons at nitrogen.

TABLE I
IR and ^{1}H NMR spectral data for compounds **1a**, **2a** and 4-methylbenzene-1-sulfonamide

Spectral data	**1a**	**2a**	*p*-Toluenesulfonamide
IR (KBr, cm^{-1})			
ν(NH), ν(NH_2)	3295	3171, 3087	3251, 3133
ν(SO_2)	1290, 1132	1373, 1179	1324, 1148
ν(C≡O)	2046, 1994	2077, 2053	–
^{1}H NMR, acetone-d_6			
Substituted phenyl	7.63, 7.25	7.83, 7.51	7.77, 7.36
Cp	5.14	5.64	–
NH (NH_2)	2.82	2.98	2.88
Me	2.37	2.46	2.40

*X-ray Crystal Structure of **2a***

The crystals of **2a** suitable for X-ray analysis were grown from layered dichloromethane–ether solution. Crystal data and structure refinement details are collected in Table II. Selected bond distances and angles are shown in Table III. The view of the molecule of **2a** is shown in Fig. 1.

The asymmetric unit of the crystal of **2a** consists of one $(C_{14}H_{14}FeNO_4S)^+$ cation and one $(BF_4)^-$ anion. In the crystal these ions form infinite chains through NH···F hydrogen bonds (Fig. 2 and Table IV).

Although **2a** crystallizes in a chiral space group the structure show local mirror plane symmetry. There is a non-crystallographic C_s symmetry of cation with pseudo-mirror plane passing through C15, the midpoint of the C12–C13 bond, Fe1, N2, S2, C21 and C24 observed. The bond lengths and angles in the cation are comparable with those of neutral molecule of the similar structure except for those involving the N2 atom[6]. In **2a**, the N2 bonds are a little longer, 2.047(5) Å for N–Fe bond and 1.691(4) Å for N–S bond, in comparison with the 4-thiocyanobenzenesulfonamido derivative – 1.965(4) and 1.565 Å, respectively.

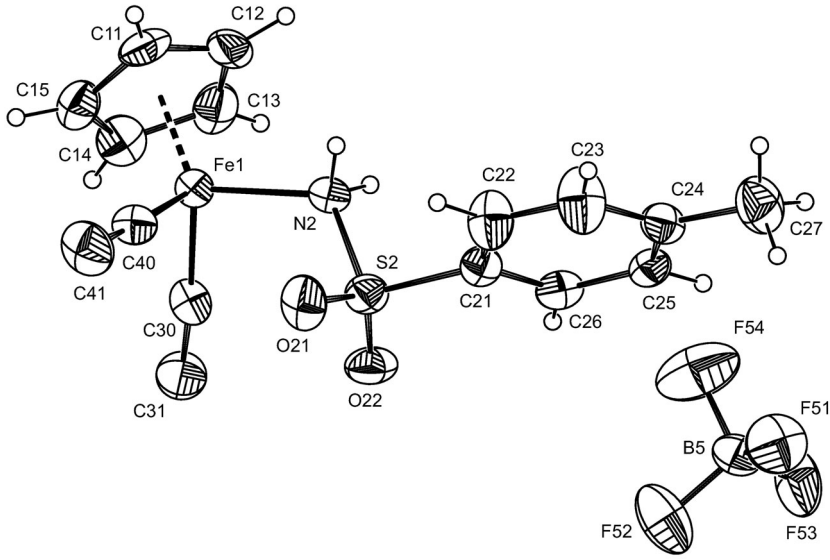

FIG. 1
View of the cation and anion of **2a** in asymmetric unit with atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at 30% probability level. Hydrogen atoms are shown as small spheres of arbitrary radii

TABLE II
Crystal data for **2a** and structure refinement details

Empirical formula	$C_{14}H_{14}BF_4FeNO_4S$
Formula weight	434.98
Crystal system, space group	orthorhombic, $P2_12_12_1$ (No. 19)
Unit cell dimensions, Å	a = 11.373(1)
	b = 16.060(1)
	c = 9.740(1)
V, Å^3	1779.0(3)
Z	4
ρ_{calc}, g cm^{-3}	1.624
Absorption coefficient, mm^{-1}	8.468
T_{min}/T_{max}	0.0951/0.3343
F(000)	880
Crystal habit	orange prism
Crystal size, mm	0.3 × 0.25 × 0.2
T, K	293(2)
Radiation type; wavelength, Å	CuKα; 1.54178
θ range for data collection, °	4.76–68.45
Limiting indices	$-13 \le h \le 13$
	$-12 \le k \le 19$
	$-8 \le l \le 11$
Reflections collected/unique	3477/3174 [R_{int} = 0.043]
Data/restraints/parameters	3174/24/215
GOF on F^2	0.907
Final R indices [$I > 2\sigma(I)$]	R = 0.0365[a], wR = 0.0600[b]
R indices (all data)	R = 0.0699[a], wR = 0.1162[b]
Largest diff. peak and hole, e Å^{-3}	0.236 and –0.249
Flack parameter	–0.015(6)
Extinction coefficient	0.0042(2)

[a] $R(F) = \Sigma(|F_o - F_c|)/\Sigma|F_o|$; [b] $wR(F^2) = [\Sigma w(|F_o - F_c|)^2/\Sigma|F_o|^2]^{1/2}$; $w = 3[(\sin\theta)/\lambda]/[\sigma^2(F_o^2) + (0.0097P)^2]$, where $P = [(F_o^2) + 2(F_c^2)]/3$.

TABLE III
Selected geometric parameters for **2a**

Bond, Å		Angle, °	
Fe1–C30	1.751(6)	C30–Fe1–C40	94.0(3)
Fe1–C40	1.780(5)	C30–Fe1–N2	98.1(2)
Fe1–N2	2.044(4)	C40–Fe1–N2	96.5(2)
Fe1–C11	2.102(3)	O22–S2–O21	121.2(3)
Fe1–C12	2.071(3)	O22–S2–N2	105.0(2)
Fe1–C13	2.070(3)	O21–S2–N2	104.6(2)
Fe1–C14	2.073(2)	O22–S2–C21	110.6(3)
Fe1–C15	2.108(2)	O21–S2–C21	109.0(2)
S2–O22	1.416(3)	N2–S2–C21	104.9(2)
S2–O21	1.425(3)	S2–N2–Fe1	120.0(2)
S2–N2	1.691(4)	O31–C30–Fe1	174.7(5)
S2–C21	1.752(5)	O41–C40–Fe1	172.8(6)
C30–O31	1.168(5)	Fe1–N2–S2–C21	175.8(3)
C40–O41	1.145(5)	Fe1–N2–S2–O22	–67.6(3)
		Fe1–N2–S2–O21	61.0(3)
		N2–S2–C21–C22	94.4(5)
		N2–S2–C21–C26	–85.5(5)
		O21–S2–C21–C22	–154.0(4)
		O21–S2–C21–C26	26.1(5)
		O22–S2–C21–C22	161.8(5)
		O22–S2–C21–C26	–18.4(5)

Moreover, some differences in molecular conformation around nitrogen atom when compared neutral and ionic structure are noticeable. For example in like to tetrahedral geometry around N atom of ionic structure Fe–N–S angle is equal 120.0(2)°, while in pyramidal geometry of the neutral molecule increasing value of 129.8(2)° is observed.

TABLE IV
Hydrogen bonding geometry (in Å and °)

D–H A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
N2–H2A···F53^{i}	0.90	1.93	2.816(4)	167
N2–H2B···F52^{ii}	0.90	1.96	2.857(4)	174

Symmetry codes: ^{i} $x - 1/2, 1/2 - y, -z$; ^{ii} x, y, z.

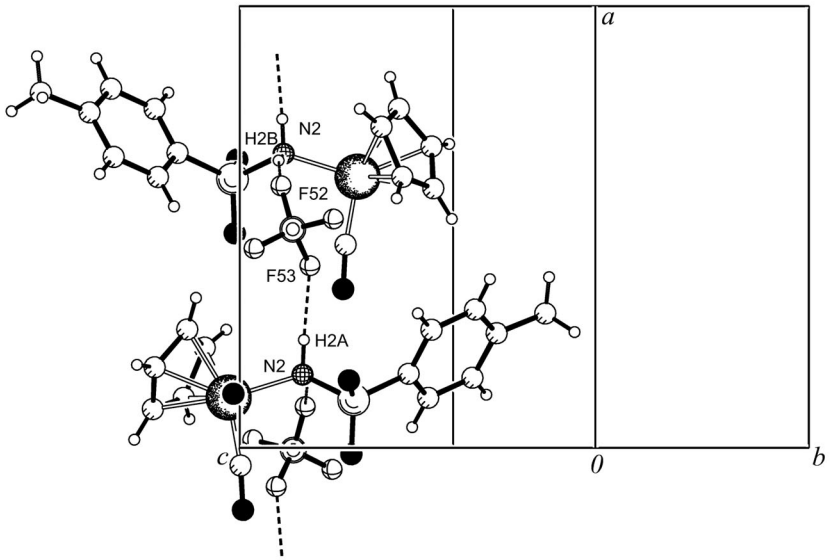

FIG. 2
The scheme of intermolecular hydrogen bonding chains in the crystal of **2a**. N–H···F interactions forming infinite chains of molecules around the 2_1 screw axis parallel to the [100] crystallographic direction are shown with dotted lines

Conclusion

We have found that the Fp(benzenesulfonamido) complexes undergo in a strongly acidic medium (HBF_4), protonation at the nitrogen atom to afford the Fp(benzenesulfonamide)$^+$ species. The protonation is reversible and protonated cationic complexes are more substitution-labile than their neutral counterparts. In the context to these results it is worthy noting that reversible protonation of a tetrazolate ligand in an Fp complex was observed by Palazzi et al.[1c] but in this case it occurred at a nitrogen atom that was not directly bound to the iron atom.

EXPERIMENTAL

Reactions using organoiron complexes were carried out under argon. ^{1}H and ^{15}N NMR spectra (δ, ppm; *J*, Hz) were recorded on a Varian 200BB spectrometer (200 MHz for ^{1}H and 20 MHz for ^{15}N) using internal TMS and external [^{15}N]-nitromethane reference, respectively. IR spectra (ν, cm^{-1}) were run on a Bio-Rad FTS-175C apparatus. Compounds **1a**, **1b** were prepared according to the earlier published procedure[7]. Benzene was distilled over Na-benzophenone immediately before use. All reagents were commercially available (Sigma–Aldrich) and were used without further purification. Kieselgel 60 (Merck, 230–400 mesh ASTM) was used for column chromatography.

Preparation of 4-Methyl[^{15}N]benzene-1-sulfonamide

To 2 ml of 6 M aqueous solution of $^{15}NH_3$, tosyl chloride (3 mmol) was added at 60 °C. The resulting mixture was refluxed for 3 h, cooled to room temperature and the solid filtered off and recrystallized from methanol–water. Yield 82%. ^{15}N NMR (DMSO-d_6): 284 t, J_{15N-H} = 84. IR ($CHCl_3$): 3435, 3341 (NH_2); 1349, 1164 (SO_2).

Preparation of [^{15}N]-**1a**

This complex was synthesized from and the 4-methyl[^{15}N]benzene-1-sulfonamide according to the earlier published procedure. ^{15}N NMR (DMSO-d_6): 397 d, J_{15N-H} = 73. IR ($CHCl_3$): 2053, 2004 (CO); 3362 (NH); 1297, 1135 (SO_2).

Preparation of Protonated Complexes **2a** and **2b**

Complexes **1a** and **1b** (0.2 mmol) were dissolved in benzene (30 ml) and treated with $HBF_4 \cdot Et_2O$ (0.3 ml) with vigorous stirring. The orange-red solutions turned immediately yellow and orange solids precipitated. The solids were filtered off, washed with benzene and diethyl ether and dried in vacuo.

2a (yield 75%): ^{1}H NMR (acetone-d_6): 7.83 d, *J* = 8.0, 2 H (arom. H); 7.51 d, *J* = 8.0, 2 H, (arom. H); 5.64 s, 5 H (Cp); 2.98 s, 2 H (NH_2); 2.46 s, 3 H (Me). IR (KBr): 2077, 2053 (CO); 3111, 3079 (NH_2); 1296, 1166 (SO_2); 1048 (BF_4). For $C_{14}H_{14}BF_4FeNO_4S \cdot 0.5H_2O$ (435.0) calculated: 37.87% C, 3.41% H, 3.15% N, 7.22% S; found: 37.87% C, 3.44% H, 3.46% N, 7.51% S.

2b (yield 68%): ^{1}H NMR (acetone-d_6): 8.48 d, J = 9.0, 2 H (arom. H's); 8.21 d, J = 9.0, 2 H (arom. H's); 5.62 s, 5 H (Cp); 2.88 s, 2 H (NH_2). IR (KBr): 2066, 2020 (CO); 3142, 3070 (NH_2); 1534, 1380 (NO_2); 1363, 1187 (SO_2); 1039 (BF_4). For $C_{13}H_{11}BF_4FeN_2O_6S$ (465.2) calculated: 33.57% C, 2.38% H, 6.02% N, 6.89% S; found: 33.51% C, 2.63% H, 5.62% N, 6.42% S.

Reaction of **2b** with Halide Ions

The complex **2b** (8.5 mg, 0.018 mmol) was dissolved in acetone (1 ml) containing LiCl, LiBr or KI (0.06 mmol). After 2.5 h at room temperature the solvent was evaporated to dryness and the residue triturated with chloroform (3 ml). The insoluble solid was filtered off, washed with water and dried. This material was identified, by spectral comparison with an authentic sample as 4-nitrobenzene-1-sulfonamide. The filtrate was chromatographed (SiO_2, chloroform) to afford the corresponding Fp halide (identified by comparison with an authentic sample) in practically quantitative yield.

X-ray Structure Determination

X-ray data were collected on a Rigaku AFC5S diffractometer[8] using CuKα X-ray source and a graphite monochromator. The unit cell dimentions were obtained from a least-squares fit to setting angles of 25 reflections. Analytical absorption correction was applied[9]. The structure was solved by direct method using program Crystal Structure[10] and refined by the full-matrix least-square method using SHELXL97 [11]. The fluoride atoms show large anisotropic displacement parameters, which can mask some kind of disorder in the BF_4^- anion. The hydrogen atoms were introduced in calculated positions with idealized geometry except for H2A and H2B atoms which were found in the Fourier difference map. In the final step of the refinement procedure, all non-hydrogen atoms were refined with anisotropic displacement parameters and all the hydrogen atoms were refined using a rigid body model. The molecular geometry was calculated by PARST [12] and WinGX [13]. Selected bond distances and angles are summarized in Table II. The drawings were made by program PLATON [14]. A summary of crystallographic data is given in Table I.

CCDC 299656 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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