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Synthesis and characterization of novel derivatives of *N*-(ferrocenesulfonyl)carbamic acid. X-ray structure determination of ferrocenesulfonamide and *N*-(ferrocenesulfonyl)-*N′*-butylurea

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Abstract

Ferrocenesulfonamide, **1**, was converted to novel *N*-(ferrocenesulfonyl)ureas and *N*-(ferrocenesulfonyl)carbamates via reacting **1** with the corresponding organic isocyanates or chloroformic acid esters. The molecular structures of **1** and *N*-(ferrocenesulfonyl)-*N′*-butylurea were determined by single-crystal X-ray diffraction. Crystal data: **1**: monoclinic, $P2_1/c$, with unit cell dimensions $a = 12.563(1)$, $b = 9.977(2)$, $c = 8.557(1)$ Å, and $\beta = 98.71(1)°$, $V = 1060.2(3)$ Å^3, $Z = 4$; **3e**: orthorombic, *Pbca*, $a = 9.278(1)$, $b = 15.892(4)$, $c = 22.043(3)$ Å, and $V = 3250.2(10)$ Å^3, $Z = 8$. In both **1** and **3e,** the Fe–C distances of the substituted Cp ring follow a special sequence, the Fe–C(S) bonds being shorter than the Fe–C bonds with the neighboring or remote C atoms.
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Keywords: Ferrocene; Sulfonylureas; Sulfonylcarbamates; X-ray structure

1. Introduction

Metallocenes continue to be a major research area in organometallic chemistry, as demonstrated by the high output of communications devoted to synthetic, structural and mechanistic studies, concentrating largely on ferrocene derivatives. One of the most extensively studied subjects is the synthesis of ferrocene-based phosphine ligands and their application in catalytic reactions [1]. In this context the interaction of substituents on the Cp rings with the metallic center in the same molecule is of considerable interest, as demonstrated by recent X-ray studies [2]. Search for biologically active ferrocene derivatives has also attracted considerable attention [3].

Ferrocenesulfonic acids and their derivatives are useful starting materials in various organometallic syntheses [4–6]. Abramovich et al. have studied the thermal decomposition of ferrocenesulfonyl azides [7]. No information is, however, available on the synthetic possibilities related to ferrocenesulfonamides, although the corresponding benzene, thiophene and pyridine sulfonamides have widespread application in pharmaceutical and agricultural chemistry. Sulfanilamide-based drugs and *N*-arylsulfonyl-*N′*-alkylureas have been used over several decades in human therapeutics. Discovery of the excellent herbicidal activity of certain *N*-arylsulfonyl-*N′*-heteroarylureas in the mid 1970's initiated extensive research and led to the development of more than a dozen highly efficient sulfonylurea type herbicides [8].

In an attempt to help explore the possible synthetic potential of ferrocene-based sulfonamide derivatives, we have prepared and characterized a number of ferrocenesulfonylureas and ferrocenesulfonylcarbamates. In this paper we report the synthesis and spectroscopic properties of these compounds together with the crystal and molecular structure of ferrocenesulfonamide and *N*-ferrocenesulfonyl-*N′*-butylurea.

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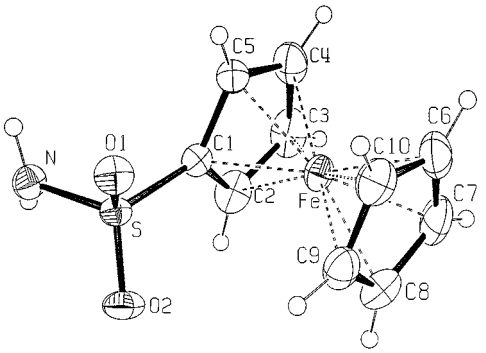

Fig. 1. Molecular diagram for ferrocenesulfonamide (**1**) with the numbering of atoms. Thermal ellipsoids represent 40% probabilities. The centroids of the Cp rings are defined as X(1)[C(1),C(2),C(3),C(4),C(5)] and X(2)[C(6),C(7),C(8),C(9),C(10)]. X(1)–Fe–X(2) = 179.3 °, C(1)–X(1)–X(2)–C(9) = 5.8°.

2. Results and discussion

Ferrocene is susceptible to electrophilic substitution and the presence of an electron-withdrawing substituent generally does not prevent the molecule from a second electrophilic reaction in the unsubstituted Cp ring. Although chlorothioformic acid esters have been reported to form ferrocenethiocarboxylic acid S-esters in reactions mediated by $AlCl_3$ [9], we did not observe C-acylation under non-catalytic conditions.

In the ^{1}H-NMR spectra of compounds **3a–k** the four protons of the substituted cyclopentadienyl ring form an AA′BB′ system, while the hydrogen atoms of the other Cp moiety appear as a sharp singlet. The protons attached to the sulfonamide nitrogen atoms show up between 7.1 and 7.6 ppm as broadened resonances. The position of the other N-bound H-atom depends on the nature of the R substituent. It is located around 6.4–6.5 ppm for R = alkyl groups and poorly resolved couplings to the *vicinal* hydrogen atoms can be observed. The same protons in the *N*′-arylureas appear in the region of 8.4–8.7 ppm reflecting an upfield shift caused by the aromatic ring.

To our knowledge, there are only two communications devoted to the crystallographic characterization of ferrocenesulfonic acid derivatives. Beside an early study [10] on the structure of 1,1′-ferrocenedisulfonyl chloride (recomputed in 1964) [11], the Cambridge Crystallographic Data Centre File contains only the related structure of ferrocenesulfonyl azide [7]. We now describe the crystal and molecular structure of ferrocenesulfonamide, **1**, and *N*-ferrocenesulfonyl-*N*′-butylurea, **3e**.

The Fe–C distances in **1** range from 2.010(1) to 2.055(2) Å with mean values of 2.039 Å for the substituted, and 2.042 Å for the unsubstituted Cp ring, respectively, in good agreement with the average Fe–C bond length in ferrocene (2.031 Å) [12]. The mean C–C bond length in the unsubstituted ring is 1.413 Å (1.402 Å in ferrocene [12]) and the C–C–C angles vary only by a few tenths of a degree (107.8–108.4°) around the theoretical value of 108°. The presence of the aminosulfonyl substituent in the other Cp ring leads to deformation reflected by the larger interval of the C–C–C angles (106.8–108.7°) and also to some elongation of the C(1)–C(2) and C(1)–C(5) bonds but exerts only a negligible effect on the mean C–C distance (1.420 Å).

The average S–O (1.434 Å) and the N–S bond distances (1.608 Å) are in good agreement with the respective values observed for *p*-toluenesulfonamide [13] (1.431 and 1.610 Å). The C(1)–S bond (1.743 Å), however, is appreciably shorter than the corresponding value in *p*-toluenesulfonamide (1.788 Å).

The bonds around the sulfur atom are disposed in a distorted tetrahedral arrangement with angles very similar to those observed in *p*-toluenesulfonamide. The sulfur atom lies in the plane determined by the carbon atoms of the cyclopentadienyl ring to which it is attached ($\Sigma\varphi$ (C1) = 360°).

In the crystal structure of **1** (Fig. 1), the hydrophobic parts of the molecules form a layer stabilized by van

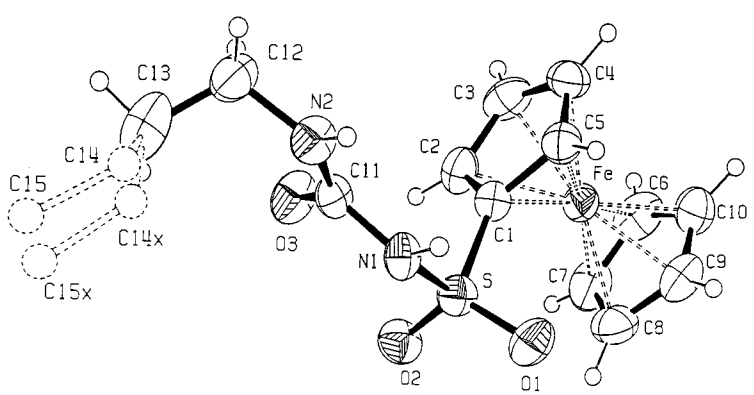

Fig. 2. Molecular diagram for **3e** with the numbering of atoms. Thermal ellipsoids represent 40% probabilities. The disordered atoms are drawn as spheres and the hydrogen atoms linked to them are omitted for clarity. The centroids of the Cp rings are defined as X(1)[C(1),C(2),C(3),C(4),C(5)] and X(2)[C(6),C(7),C(8),C(9),C(10)]. X(1)–Fe–X(2) = 178.4 °, C(1)–X(1)–X(2)–C(8) = 6.6°.

Table 1
Selected spectroscopic data of compounds **3a–k**

Compound	^{1}H-NMR					IR (KBr, cm^{-1})
	*N*H	*N*′H	Aliphatic protons	Cp, substituted[a]	Cp, free[b]	
3a	7.46 (br)	8.42	—	4.72; 4.46	4.44	3327, 1679, 1600, 1547, 1351, 1126
3b	7.24 (br)	8.46	—	4.70; 4.48	4.44	3327, 1703, 1605, 1553, 1492, 1349, 1126, 1118
3c	7.57	8.62	—	4.71; 4.48	4.45	3350, 1696, 1566, 1347, 1337, 1167, 1128
3d	7.10	6.45(br)	2.83 (3H, d, 4.8 Hz)	4.67; 4.45	4.43	3331, 1656, 1549, 1349, 1195, 1141
3e	7.60	6.50(br)	3.22 (2H, d/t, 5.7 Hz, 7.1 Hz), 1.49 (2H, m); 1.34 (2H, m), 0.95 (3H, t, 7.3 Hz)	4.64; 4.43	4.42	3341, 1659, 1550, 1344, 1196, 1141
3f	7.32 (br)	6.41 (br, d, 7.9 Hz)	3.62 (1H, m), 1.91 (2H), 1.70 (2H), 1.59 (2H), 1.35 (2H) and 1.20 (2H) (all multiplets)	4.66; 4.44	4.42	3333, 1649, 1550, 1343, 1196, 1142
3g	7.47 (br)	—	2.90 (6H, s)	4.88; 4.44	4.41	3266, 1684, 1431, 1361, 1331, 1201, 1124
3h	7.28 (br)[c]	—	4.14 (2H, q, 7.1 Hz), 1.24 (3H, t, 7.1 Hz)	4.83; 4.47	4.43	3300–2800(br), 1704(br)[e], 1478, 1432, 1381, 1362, 1312, 1203, 1142
3i	—[d]	—	5.10 (2H, s)	4.79; 4.43	4.41	3240(br), 1756, 1744[e], 1436, 1348, 1227, 1132
3j	Not recorded	—	—	—	—	3240, 1760, 1450, 1345, 1220, 1150
3k	7.48	12.60	2.43 (6H, s), 6.71 (1H, s)[f]	4.92; 4.43	4.44	3400–2850, 1710(sh), 1700, 1595, 1445(br), 1330, 1130

[a] AA′BB′ multiplets, 2-2 H; [b] 5 H, s; [c] at 70°C: 7.08 ppm; [d] covered by aromatic protons; [e] $\nu_{CO} = 1750$ cm^{-1} in 7 mg ml^{-1} CCl_4 solution; [f] pyrimidine C*H*.
s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

der Waals interactions, while the aminosulfonyl moieties constitute another plane in which the NH_2 group of molecule A and the sulfonyl group of molecule B are connected by hydrogen bonds (respective distances and angles are shown in Table 5). One of the hydrogen atoms [H(1)N] is obviously involved in a bifurcated H-bond system ($\Sigma\varphi$ (H1N) = 356.1°) [14]. H(2)N maintains only a week interaction with O(2).

In **3e**, the average Fe–C distances in the substituted (2.035 Å) and in the unsubstituted Cp ring (2.038 Å) are practically equal. These numbers hide the fact, however, that the individual Fe–C bonds in the unsubstituted Cp moiety are far more uniform (2.031–2.047 Å) than they are in its sulfonylated counterpart (1.998–2.057 Å). The mean C–C distance is but slightly longer in the substituted (1.410 Å) than in the unsubstituted ring (1.400 Å) due to the presence of the electron-withdrawing substituent. The crystal structure **3e** (Fig. 2) does not seem to follow the reported trend (valid also for **1**) that the longest C–C bonds in Cp rings involve the substituted carbon atom [15]. However, this difference may only be apparent as the estimated S.D. of the C–C bonds in **3e** are twice as great as those observed for **1**.

The bond lengths of the sulfur atom with O(1), O(2) and C(1) are about the same in **1** and **3e**. The wide interval of angles around S (103.4–120.4°) reflects a distorted tetrahedral arrangement of the atoms involved. The N(1)–S bond is longer by 0.05 Å in **3e** than that in **1**. This feature may be attributed to the strong electron-withdrawing effect of the carbonyl group, which reduces the ability of N(1) to donate electrons to the sulfonyl group, thereby decreasing the N(1)–S bond order. The length of the N(1)–S bond (1.656 Å) in **3e** is comparable with the corresponding bond lengths in tolbutamide [*N*-*p*-toluenesulfonyl-*N*′-*n*-butylurea] [16] (1.653 Å) and chlorpropamide [*N*-*p*-chlorobenzenesulfonyl-*N*′-*n*-propylurea] [17] (1.644 Å). The difference between the N(2)–C(11) and N(1)–C(11) bonds is in line with the larger electron density localized on N(2) compared with that on N(1). The value of 1.223 Å is typical for C=O double bonds.

The crystal structure of **3e** is stabilized by both van der Waals interactions and hydrogen bonds. The proximity of N(2) and O(3′) as well as N(2) and one of the sulfonyl oxygen atoms of a neighboring molecule (see Table 5) indicates that hydrogen bond formation is feasible. The sum of angles about HN(2) is 358.0°,

which satisfies the requirement for bifurcated hydrogen bonds [14]. The proton attached to the sulfonyl nitrogen interacts only with a carbonyl oxygen. Similar stabilizing interactions have been observed in the structure of the *p*-tosyl analogue [16], while the structural analysis of chlorpropamide [17] revealed the presence of only two types of hydrogen bonds.

Although many structural properties of ferrocene-1,1′-disulfonyl chloride [11], ferrocenesulfonyl azide [7] as well as **1** and **3e** can be regarded as typical to ferrocene derivatives, they also display some unexpected features. These ''irregularities'' involve the sulfonyl group and its neighborhood.

The S–C bonds of both sulfonyl groups in ferrocene-1,1′-disulfonyl chloride are bent by 5.5° toward the Cp ring to which they are not attached. This phenomenon was ascribed to the interaction of neighboring molecules in the crystal lattice.

McManus et al. [7] noticed that in the solid state structure of ferrocenesulfonyl azide the Fe atom is ''slightly offset toward the sulfonyl azide group'' and postulated a weak bonding interaction ''between a metal d orbital and either of the oxygens or an empty sulfur d orbital''.

In both **1** and **3e**, the Fe–C distances follow a particular order, namely Fe–C(4) ≅ Fe–C(3) > Fe–C(5) ≅ Fe–C(2) > Fe–C(1). Such sequence of bond lengths indicate that an interaction between the sulfonyl group and the iron atom may exist which causes a slight distortion of the structure, as has been supposed for ferrocenesulfonyl azide [7]. Taking into account that the Fe–O(1) and Fe–O(2) distances (**1**: 3.739 and 3.713 Å; **3e**: 3.601 and 3.846 Å) are by far longer than the Fe–S distances (**1**: 3.344 Å; **3e**: 3.298 Å), a $d\pi$–$d\pi$ interaction between the iron and sulfur atoms seems to be more likely. In our view, the observed displacement of sulfur atoms in ferrocenedisulfonyl chloride may also be attributed to a weak sulfur to iron bonding of this type.

Bonding interactions of the iron center with electron deficient substituents on the Cp ring {CR_2^+ [18,19], BBr_2 ([2]a)} are well documented. Similar forces seem to affect the geometry of the sulfonated ferrocenes discussed here and in the communications cited although the strength of the Fe–S interaction is influenced by the substituents attached to the sulfonyl group.

Table 2
Experimental data for the X-ray diffraction studies on compounds **1** and **3e**

	1	**3e**
Empirical formula	$C_{10}H_{11}FeNO_2S$	$C_{15}H_{20}FeN_2O_3S$
Formula weight	265.11	364.24
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pbca*
Unit cell dimensions		
a (Å)	12.563(1)	9.278(1)
b (Å)	9.977(2)	15.892(4)
c (Å)	8.557(1)	22.043(3)
β (°)	98.71(1)	—
Volume (Å^3)	1060.2(3)	3250.2(10)
Z	4	8
$D_{calc.}$ (mg/m^3)	1.661	1.489
Absorption coefficient, μ (mm^{-1})	1.595	1.069
F(000)	544	1520
Crystal color	Yellow	Orange
Crystal description	Block	Block
Crystal size (mm)	0.40 × 0.30 × 0.15	0.20 × 0.25 × 0.35
Index ranges	$-22 \le h \le 22$; $-7 \le k \le 17$; $0 \le l \le 15$	$-7 \le h \le 11$; $-20 \le k \le 8$; $-12 \le l \le 28$
θ range (°)	2.62–39.74	2.56–27.05
Reflections collected	7508	3663
Independent reflections	6459 [R_{int} = 0.0128]	3564 [R_{int} = 0.0292]
Absorption correction	Empirical (Ψ-scans)	Empirical (Ψ-scans)
Min./max. transmission factors	0.826/1.000	0.900/1.000
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5153/0/138	3492/46/223
Goodness-of-fit on F^2	1.021	0.829
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0368$, $wR_2 = 0.0946$	$R_1 = 0.0448$, $wR_2 = 0.1088$
R indices (all data)	$R_1 = 0.1043$, $wR_2 = 0.1243$	$R_1 = 0.1090$, $wR_2 = 0.1426$
Largest difference peak and hole (e Å^{-3})	0.503 and −0.575	0.654 and −0.286

Table 3
Selected bond distances (Å) and angles (°) for compound **1**

Bond length (Å)			
Fe–C(1)	2.010(1)	Fe–C(7)	2.034(2)
Fe–C(2)	2.038(2)	Fe–C(8)	2.040(2)
Fe–C(6)	2.041(2)	Fe–C(5)	2.041(2)
Fe–C(10)	2.044(2)	Fe–C(3)	2.049(2)
Fe–C(9)	2.050(2)	Fe–C(4)	2.055(2)
N–S	1.608(1)	S–O(2)	1.428(1)
S–O(1)	1.440(1)	S–C(1)	1.743(1)
C(1)–C(2)	1.428(2)	C(1)–C(5)	1.431(2)
C(2)–C(3)	1.420(3)	C(3)–C(4)	1.406(3)
C(4)–C(5)	1.417(2)	C(6)–C(7)	1.401(3)
C(6)–C(10)	1.418(3)	C(7)–C(8)	1.419(3)
C(8)–C(9)	1.421(3)	C(9)–C(10)	1.404(3)
Bond angle (°)			
O(2)–S–N	106.8(1)	O(1)–S–C(1)	107.1(1)
O2–S–C(1)	108.1(1)	C(2)–C(1)–C(5)	108.5(1)
N–S–C(1)	107.9(1)	C(5)–C(1)–S	125.4(1)
C(2)–C(1)–S	126.1(1)	C(3)–C(4)–C(5)	108.7(2)
O(1)–S–N	107.0(1)	C(3)–C(2)–C(1)	106.8(2)
O(2)–S–O(1)	119.4(1)	C(7)–C(6)–C(10)	108.4(2)
C(4)–C(3)–C(2)	108.9(2)	C(7)–C(8)–C(9)	107.9(2)
C(4)–C(5)–C(1)	107.0(2)	C(9)–C(10)–C(6)	108.1(2)
C(6)–C(7)–C(8)	107.8(2)	C(10)–C(9)–C(8)	107.8(2)

Table 4
Selected bond distances (Å) and angles (°) for compound **3e**

Bond length (Å)			
Fe–C(1)	1.998(3)	Fe–C(7)	2.031(4)
Fe–C(8)	2.035(4)	Fe–C(2)	2.035(3)
Fe–C(5)	2.039(3)	Fe–C(6)	2.039(4)
Fe–C(9)	2.038(4)	Fe–C(10)	2.047(4)
Fe–C(3)	2.046(4)	Fe–C(4)	2.057(4)
S–O(1)	1.423(2)	S–O(2)	1.424(3)
S–N(1)	1.656(3)	S–C(1)	1.737(4)
O(3)–C(11)	1.223(4)	N(1)–C(11)	1.393(4)
N(2)–C(11)	1.328(4)	N(2)–C(12)	1.443(5)
C(1)–C(2)	1.410(4)	C(1)–C(5)	1.429(5)
C(2)–C(3)	1.404(5)	C(3)–C(4)	1.390(6)
C(4)–C(5)	1.419(5)	C(6)–C(10)	1.400(6)
C(6)–C(7)	1.412(6)	C(7)–C(8)	1.405(6)
C(8)–C(9)	1.396(6)	C(9)–C(10)	1.386(6)
C(12)–C(13)	1.480(7)	C(13)–C(14)	1.498(5)
C(13)–C(14)x	1.504(5)	C(14)–C(15)	1.513(5)
C(14)x–C(15)x	1.510(5)		
Bond angle (°)			
O(1)–S–N(1)	103.4(2)	O(1)–S–O(2)	120.4(2)
O(1)–S–C(1)	110.3(2)	O(2)–S–N(1)	109.0(2)
N(1)–S–C(1)	104.5(2)	O(2)–S–C(1)	108.1(2)
C(11)–N(2)–C(12)	121.3(3)	C(11)–N(1)–S	121.5(2)
C(2)–C(1)–S	127.0(3)	C(2)–C(1)–C(5)	108.8(3)
C(2)–C(3)–C(4)	109.6(3)	C(5)–C(1)–S	124.2(3)
C(4)–C(5)–C(1)	106.4(3)	C(3)–C(4)–C(5)	108.3(3)
C(6)–C(7)–C(8)	107.9(4)	C(3)–C(2)–C(1)	106.9(3)
C(8)–C(9)–C(10)	108.5(4)	C(10)–C(6)–C(7)	107.3(4)
O(3)–C(11)–N(2)	124.3(3)	C(9)–C(8)–C(7)	107.7(4)
N(2)–C(11)–N(1)	114.6(3)	C(6)–C(10)–C(9)	108.6(4)
C(12)–C(13)–C14	113.7(5)	O(3)–C(11)–N(1)	121.1(3)
C(13)–C(14x) –C(15x)	109(2)	N(2)–C(12)–C(13)	114.1(4)
C(13)–C(14)–C(15)	115.9(7)	C(12)–C(13)–C(14x)	114.4(7)

In summary, we have found $FcSO_2NH_2$ to be a convenient starting material for the synthesis of various derivatives of ferrocenesulfonylcarbamic acids. Both ferrocenesulfonamide and *N*-ferrocenylsulfonyl-*N'*-butylurea exhibit the structural features of arylsulfonic acid derivatives and, unless other factors interfere, ferrocenesulfonamide may be potential starting material for biologically active compounds. Further studies are needed to determine if the structural features of ferrocenesulfonic acid derivatives discussed in this work are common also to other sulfonated metallocenes.

3. Experimental section

Ferrocenesulfonic acid ($FcSO_3H$) was prepared according to a literature procedure [6] and isolated as its *p*-toluidine salt. The latter was converted to ferrocenesulfonyl chloride [6] which, in turn, gave ferrocenesulfonamide, **1**, upon treatment with NH_3 in benzene. **1** served as starting material in the syntheses of carbamic acid derivatives. Experiments with organic isocyanates R1NCO (**2a–f**), *N*,*N*-dimethylcarbamoyl chloride (**2g**) and chloroformic acid derivatives $ClC(O)OR^2$ (**2h–j**) were carried out with the exclusion of moisture.

*3.1. Synthesis of $FcSO_2NHC(O)NHR^1$ (**3a–f**); [**3a**, R^1 = phenyl; **3b**, R^1 = p-Cl-phenyl; **3c**, R^1 = m-CF_3-phenyl; **3d**, R^1 = methyl; **3e**, R^1 = butyl; **3f**, R^1 = cyclohexyl]*

A total of 10 mmol of $FcSO_2NH_2$ and 10 mmol of dried K_2CO_3 were added to 60 ml dry acetone, and 13 mmol of each aryl isocyanate **2a–c** was introduced dropwise. The reaction mixture was stirred for 4 h at ambient temperature, while the original brownish color turned yellow. The slurry was poured into 100 ml of water, the white precipitate of $(R^1NH)_2C(O)$ was removed by filtration, and the filtrate was acidified to pH = 4 by adding 1M HCl solution. The yellow product was collected on a filter, washed with water and dried. Recrystallization from ethyl acetate gave pure ureas in 60–70% yield.

3d–f were prepared in an analogous way at reflux temperature.

Elemental analysis: **3a** Calc. for $C_{17}H_{16}FeN_2O_3S$: C 53.14, H 4.20, N 7.29, S 8.34, found: C 53.29, H 4.25,N 7.22, S 8.08; **3b** Calc. for $C_{17}H_{15}ClFeN_2O_3S$: C 48.77, H 3.61, N 6.69, S 7.66, found: C 48.89, H 3.68, N 6.80, S 7.55; **3c** Calc. for $C_{18}H_{15}F_3FeN_2O_3S$: C 47.81, H 3.34, N 6.19, S 7.09, found: C 47.60, H 3.43, N 6.09, S 6.95; **3d** Calc. for $C_{12}H_{14}FeN_2O_3S$: C 44.74, H 4.38, N 8.70, S 9.95, found: C 44.64, H 4.15, N 8.78, S 9.93; **3e** Calc. for $C_{15}H_{20}FeN_2O_3S$: C 49.46, H 5.53, N 7.69, S 8.80, found: C 49.28, H 5.46, N 7.74, S 8.64; **3f** Calc. for $C_{17}H_{22}FeN_2O_3S$: C 52.32, H 5.68, N 7.18, S 8.22, found: C 52.17, H 5.76, N 7.30, S 8.18%.

MS data: **3d** (FAB): 323 $(M+H)^+$, 322 (M^+); **3e** [EI, 70 eV)]: 364 (M^+) (22), 291 (24), 265 (100).

*3.2. Synthesis of $FcSO_2NHC(O)N(CH_3)_2$ (**3g**) and $FcSO_2NHC(O)OR^2$ (**3h–j**) [**3h**, R^2 = ethyl; **3i**, R^2 = benzyl; **3j**, R^2 = phenyl]*

Compounds **3g–j** were synthesized using *N*,*N*-dimethylcarbamoyl chloride (**2g**) or chloroformic acid esters $ClC(O)OR_2$ (**2h–j**), as described above, but the reactions were conducted at r.t. for 48 h.

*3.3. $FcSO_2NHC(O)NH$(4,6-dimethylpyrimidin-2-yl) (**3k**)*

Compound **3k** was prepared by refluxing 5 mmol of **3j** and 5 mmol of 2-amino-4,6-dimethylpyrimidine in 30 ml of dry acetonitrile for 3 h. After all the phenylcarbamate had been converted, the reaction mixture was concentrated to half volume and the product was filtered. Recrystallization yielded 50% of **3k**.

Table 5
Hydrogen bonds in compounds **1** and **3e**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
Compound **1**				
N–H(1)N···O(1)[a]	0.880	2.208	3.063	164.0
N–H(1)N···O(2)[b]	0.880	2.534	2.855	102.4
N–H(2)N···O(2)[b]	0.919	2.438	2.855	107.7
Compound **3e**				
N(1)–HN(1)···O(3)[c]	0.943	1.903	2.808	160.3
N(2)–HN(2)···O(2)[c,d]	0.922	2.353	3.136	142.6
N(2)–HN(2)···O(3)[c,d]	0.922	2.322	3.075	138.8

[a] $-x,-y,-z+1$; [b] $x,-0.5-y,(-0.5+z)+1$; [c] $(-0.5+x)+1,y,(0.5-z)+1$; [d] bifurcated.

Elemental analysis: **3g** Calc. for $C_{13}H_{16}FeN_2O_3S$: C 46.44, H 4.80, N 8.33, S 9.54, found: C 46.60, H 4.77, N 8.40, S 9.41; **3h** Calc. for $C_{13}H_{15}FeNO_4S$: C 46.31, H 4.48, N 4.15, S 9.51, found: C 46.11, H 4.43, N 4.21, S 9.12; **3i** Calc. for $C_{18}H_{17}FeNO_4S$: C 54.15, H 4.29, N 3.51, S 8.03, found: C 53.79, H 4.19, N 3.59, S 7.79; **3k** Calc. for $C_{17}H_{18}FeN_4O_3S$: C 49.29, H 4.38, N 13.52, S 7.74, found: C 49.28, H 4.40, N 13.60, S 7.80%.

MS data: **3g** (FAB): 337 $(M+H)^+$, 336 (M^+); **3h** (EI): 337 (M^+) (13), 291 (100), 265 (23), 227 (16), 184 (18); **3i** (FAB): 400 $(M+H)^+$, 399 (M^+); **3k** (FAB): 415 $(M+H)^+$, 291.

^{1}H-NMR spectra were recorded on a Varian VXR-400 instrument in $CDCl_3$. IR spectra were measured using KBr pellets on a Nicolet 205 FT-IR spectrometer.

Selected ^{1}H-NMR and IR spectroscopic data of compounds **3a–k** are listed in Table 1.

*3.4. X-ray structure determination of $FcSO_2NH_2$ (**1**) and $FcSO_2NHC(O)NH(n\text{-butyl})$ (**3e**)*

The determination of the unit cells and intensity data collections were performed on an Enraf-Nonius CAD4 diffractometer (Mo–K_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). Data collection and least-squares parameters are given in Table 2. Cell parameters were determined by least-squares of the setting angles of 25 (**1**: $20.70 \leq \theta \leq 22.10°$; **3e**: $15.09 \leq \theta \leq 16.71°$) reflections. Backgrounds were measured at half the total time of the peak scans. The intensities of three standard reflections were monitored regularly every 60 min. The intensities of the standard reflections indicated 2% decay for **1** (a decay correction was applied to the data). Both structures were solved by the heavy atom method and subsequent difference syntheses.

Hydrogen atomic positions were calculated from assumed geometries except for N-bound hydrogens that were located in difference maps. Hydrogen atoms were included in structure factor calculations but they were not refined. The riding model was applied to the H atoms. Neutral atomic scattering factors and anomalous scattering factors were taken from the International Tables for X-ray Crystallography vol. C. Experimental data for the X-ray diffraction studies, as well as selected bond lengths and angles are collected in Tables 2–5.

4. Supplementary material available

Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** and **3e** and figures depicting the unit cells of **1** and **3e** are available on request from the authors.

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