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Ferrocenes Bearing Sulfinylamino Groups

Bernd Wrackmeyer,*[a] Elena V. Klimkina,[a] Wolfgang Milius,[a] Miriam Siebenbürger,[a] Oleg L. Tok,[a] and Max Herberhold[a]

Dedicated to Professor Dr. Walter Siebert on the occasion of his 70th birthday

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1,1′-Diaminoferrocene (**2**) and 1,1′-bis(trimethylsilylamino)ferrocene (**3**) have been converted into sulfinylamines by treatment with thionyl chloride in the presence of triethylamine. In the case of **2** the 1:2 reaction affords 1,1′-bis(sulfinylamino)ferrocene (**5**) and the 1:1 reaction gives 6-amino-1-sulfinylaminoferrocene (**6**). Bis(trimethylsilylamino)ferrocene reacts with thionyl chloride in a 1:1 molar ratio to give 1-sulfinylamino-6-(trimethylsilylamino)ferrocene (**8**). In contrast, the reaction of *N*,*N*′-dilithiobis(trimethylsilylamino)ferrocene (**4**) with thionyl chloride gives the [3]ferrocenophane **9**, which contains an N–S(O)–N bridge, rather than sulfinylamines or a sulfur diimide. The molecular structures of **5** and **8** were determined by X-ray analysis. The ^{57}Fe NMR chemical shift (δ = +2597.0 ppm) for **5** indicates the strong π-acceptor properties of the NSO groups. Dynamic ^{1}H and ^{13}C NMR spectra prove the hindered rotation of the NSO group about the C–N bonds in **5**, **6** and **8**.

Introduction

The combination of the rich chemistry of ferrocenes[1] with that of sulfinylamines[2] is an attractive target. Convenient routes for the synthesis of sulfinylamines (R-NSO) start either from the corresponding primary amines (RNH_2) or from *N*-trimethylsilylamines [RN(H)-$SiMe_3$].[2] The latter approach has been successful in the case of ferrocenylsufinylamine (Fc-NSO, **1**), which has been structurally characterised in the solid state.[3] The structure of **1** in solution has been established by various physical methods, including routine NMR spectroscopy[3] and also ^{57}Fe NMR spectroscopy.[4] The synthesis of 1,1′-diaminoferrocene [fc(NH_2)$_2$, **2**][5] has recently been improved,[6] therefore access to *N*,*N*′-disubstituted derivatives of 1,1′-diaminoferrocene, such as 1,1′-bis(trimethylsilylamino)ferrocene (**3**)[6] or its dilithiated derivative **4**,[7] has become more feasible. This is mirrored by advances in the synthesis of numerous [*n*]ferrocenophanes, for example with n = 3, with various elements between the nitrogen atoms.[7–12] In the present work, we describe attempts to convert the ferrocenes **2**–**4** into sulfinylamines, aiming particularly for NMR spectroscopic studies in solution and structural characterisation in the solid state.

Results and Discussion

The reaction of **2** with thionyl chloride in the presence of an excess of triethylamine leads to the ferrocenes **5** or **6**, depending on the ratio of the starting compounds (Scheme 1). The complete conversion of **2** into 1,1′-bis(sulfinylamino)ferrocene (**5**) requires two equivalents of thionyl chloride. Complex **5** was isolated as a violet-blue, air- and moisture-sensitive solid, which gave violet crystals after recrystallisation. The 1:1 reaction affords 6-amino-1-sulfinylaminoferrocene (**6**), which, however, is contaminated with **2** and **5**. Purification by repeated crystallisation gave pure **6** as a blue powder. The availability of **5** calls for an attempt to prepare the sulfur diimide **7**. However, the reaction of **5** with KO*t*Bu in DMF[2,3] gave only **6**, most likely as the result of partial hydrolysis of **5**.

Another route to sulfinylaminoferrocenes is conceivable from the reaction of 1,1′-bis(trimethylsilylamino)ferrocene (**3**) with thionyl chloride in the presence of triethylamine (Scheme 2). The product of the 1:1 reaction, 1-sulfinylamino-6-(trimethylsilylamino)ferrocene (**8**), is formed along with a small amount of **5**, and **8** was isolated after recrystallisation as a blue crystalline solid.

N,*N*′-Dilithiation of **3** gives **4**, and its 1:1 reaction with thionyl chloride leads to the [3]ferrocenophane **9** (Scheme 3). The formation of **9** is accompanied by decomposition leading mainly to **3**. The elimination of hexamethyldisiloxane [O($SiMe_3$)$_2$] from **9** to give the sulfur diimide **7** was not observed.

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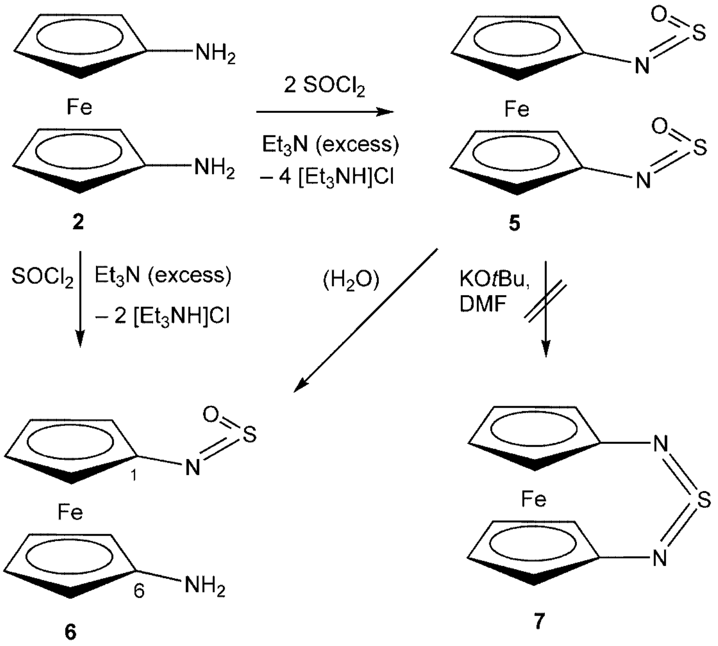
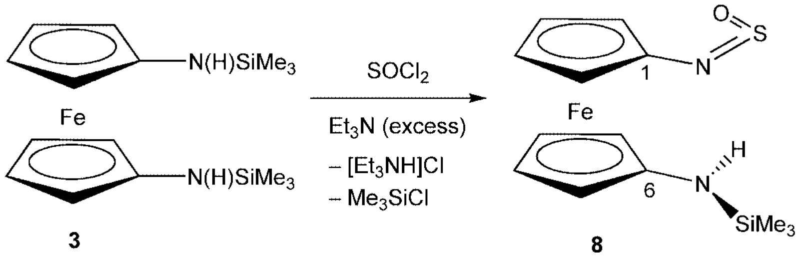
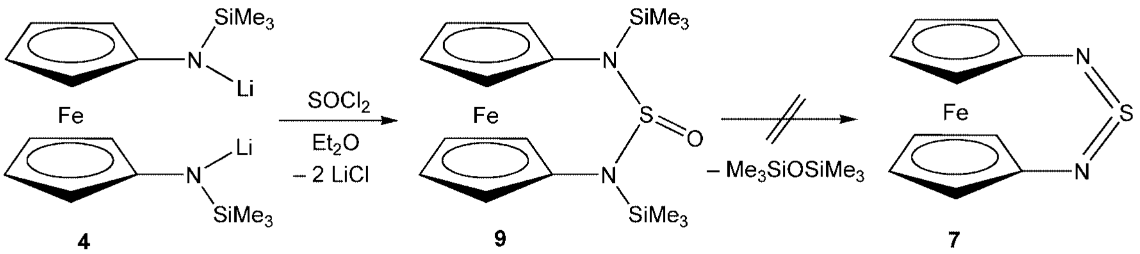
[a] Laboratorium für Anorganische Chemie, Universität Bayreuth,
95440 Bayreuth, Germany
Fax: +49-921-552157
E-mail: b.wrack@uni-bayreuth.de



Scheme 1. Reaction of 1,1′-diaminoferrocene (**2**) with thionyl chloride and attempted synthesis of the sulfur diimide **7**.



Scheme 2. Reaction of 1,1′-bis(trimethylsilylamino)ferrocene (**3**) with thionyl chloride .



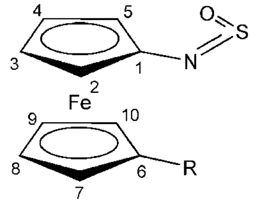
Scheme 3. Reaction of *N*,*N*′-dilithio-1,1′-bis(trimethylsilylamino)ferrocene (**4**) with thionyl chloride — another failure to obtain the sulfur diimide **7**.

NMR Spectroscopic Studies in Solution

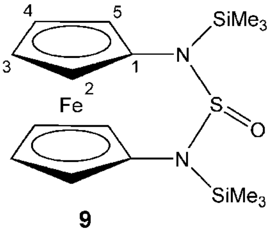
Relevant NMR spectroscopic data for the ferrocenes **1** (for comparison), **5**, **6**, **8** and **9** are given in Table 1 and in the Experimental Section (^{1}H NMR). The cyclopentadienyl groups are clearly identified by the ^{1}H and ^{13}C NMR spectroscopic data measured at room temperature. The presence of the NSO group is evident both from characteristic ^{14}N NMR signals at high frequencies[13] and the symmetric and antisymmetric NSO stretching vibrations[2] in the IR spectra. The ^{15}N NMR spectra (^{1}H coupled) prove the existence of the NH_2 and $N(H)SiMe_3$ groups in **6** and **8**, respectively. The ^{29}Si NMR signal of **8** is notably different from that of the [3]ferrocenophane **9**, and ^{29}Si nuclear deshielding is rather typical for the ring closure in **9**.[9–12]

Owing to the low NMR receptivity of ^{57}Fe nuclei, ^{57}Fe NMR spectra have rarely been reported.[14] However, careful setting of experimental parameters allows the measurement of meaningful spectra within a reasonable time.[4,15,16] The ^{57}Fe nuclear shielding in ferrocene derivatives is sensi-

Table 1. ^{13}C, ^{14}N, ^{15}N, ^{29}Si and ^{57}Fe NMR spectroscopic data[a] of compounds **1**, **5**, **6**, **8** and **9**.



1, **5**, **6**, **8**



9

Compound	**1**[3]	**5**	**6**		**8**		**9**
	R = H	R = NSO	R = NH_2		R = $N(H)SiMe_3$		
T [K]	298 K	298 K	298 K	198 K	298 K	203 K	298 K
$\delta^{13}C$ (fc-C^1)	71.2	97.3	97.4	97.8	97.8	97.7	105.7
$\delta^{13}C$ (fc-$C^{2,5}$)	69.2	70.7[b]	70.3	68.1, 71.0	70.1	66.9, 71.0	63.3, 65.1[b] 68.4, 72.3[b]
$\delta^{13}C$ (fc-$C^{3,4}$)	70.1	72.4[b]	71.4	70.2, 72.3	71.4	69.5, 72.1	
$\delta^{13}C$ (fc-C^6)	71.2	97.3	105.7	101.3	108.6	105.7	
$\delta^{13}C$ (fc-$C^{7,10}$)		70.7	59.5	57.3, 59.0	59.5	56.8, 58.6	
$\delta^{13}C$ (fc-$C^{8,9}$)		72.4	66.5	65.5, 67.4	66.4	64.7, 66.8	
$\delta^{13}C$ (Me_3Si)					–0.2 (57.1)	–1.7 (57.3)	0.3 (57.4)
$\delta^{14}N$ (NSO)	–67	–62	–57		–57		
$\delta^{15}N$			–356.4		–345.6		n.o.
$^1J(^{15}N,^1H)$ (Hz)			78.8		76.5		
$\delta^{29}Si$					6.0 (57.1)	6.5	12.0 (57.4)
$\delta^{57}Fe$	1966.3	2597.0			2131.0		

[a] Measured in $CDCl_3$ (**1**) or CD_2Cl_2 (**5**, **6**, **8** and **9**); $^1J(^{29}Si,^{13}C)$ coupling constants (±0.5 Hz) are given in parentheses; n.o. = not observed. [b] Assignment might be reversed.

tive to π-acceptor substituents, and deshielding is usually observed if the ferrocene structural geometry remains fairly undistorted.[4,16] According to the $\delta^{57}Fe$ value of **1**, the NSO group is a strong π-acceptor; this is also supported by the molecular structure of **1**, where the planes of the NSO group and the substituted cyclopentadienyl rings almost coincide.[3] Frequently, the contributions to ^{57}Fe nuclear shielding in ferrocenes are approximately additive for any substituents in 1,1′-positions.[17] Thus, the rather extreme ^{57}Fe nuclear deshielding observed for **5** ($\delta^{57}Fe$ =

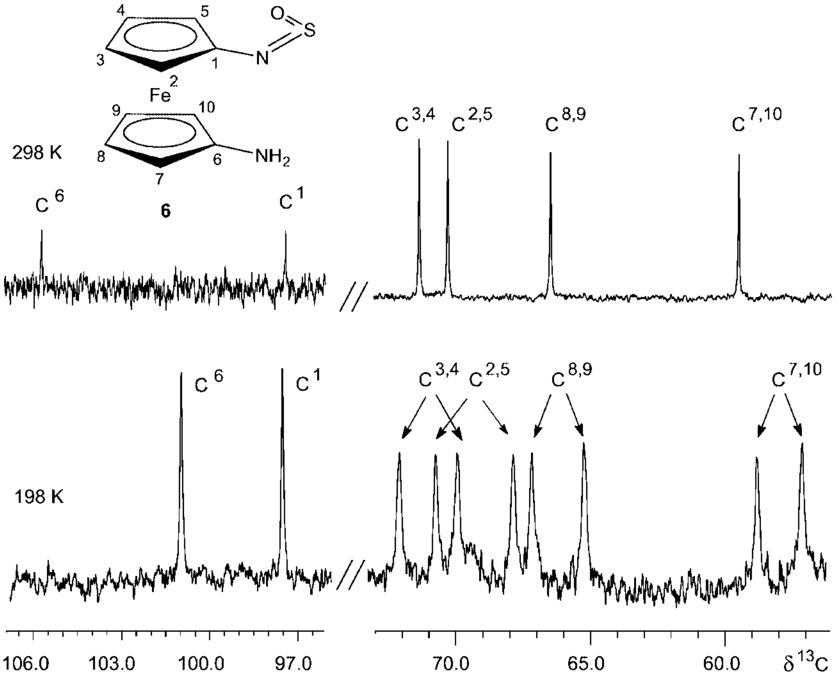


Figure 1. 62.9 MHz $^{13}C\{^1H\}$ NMR spectra of **6** at 298 K (upper trace) and 198 K (lower trace).

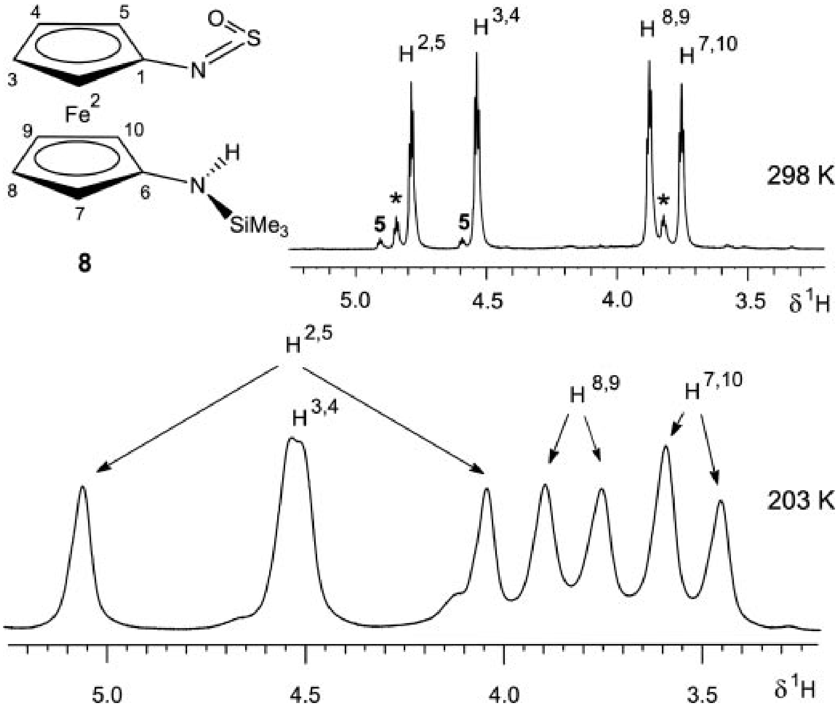


Figure 2. Parts of the 250.1 MHz ^{1}H NMR spectra of the ferrocene **8** at 298 K (upper trace) and 203 K (lower trace). Signals of a side product are marked with asterisks.

+2597.0 ppm), when compared with ferrocene itself (δ^{57}Fe = +1538.4 ppm[15]), is expected; the δ^{57}Fe value for **8** (δ^{57}Fe = +2131.0 ppm) is close to that of **1** (δ^{57}Fe = +1966.3 ppm).

The π-acceptor properties of the NSO group should be reflected by restricted rotation about the C^1–N or C$^{1'}$-N bonds. Indeed, this is evident from the low-temperature ^{1}H and ^{13}C NMR spectra (Table 1, Figure 1 and Figure 2). In the case of **5**, the ^{1}H and ^{13}C NMR signals become broad at low temperature just before the complex crystallises, and in the cases of **6** and **8**, splitting of the C^{2,5}-H and C^{3,4}-H NMR signals into two signals each is observed (Figure 1 and Figure 2). In the cases of **6** and **8**, the barrier to rotation about the C^1–N(SO) bond can be estimated[18] as 43.0 ± 1 kJ mol^{-1} at –65 °C (coalescence) from both ^{1}H and ^{13}C NMR spectra. The preferred orientation of the NSO group at low temperature is also indicated by the changes in the positions of the ^{13}C^6 NMR signals in **6** and **8**.

X-ray Structural Studies of the Sulfinylaminoferrocenes 5 and 8

The molecular structures of **5** and **8** are shown in Figures 3 and 4, respectively, and selected structural param-

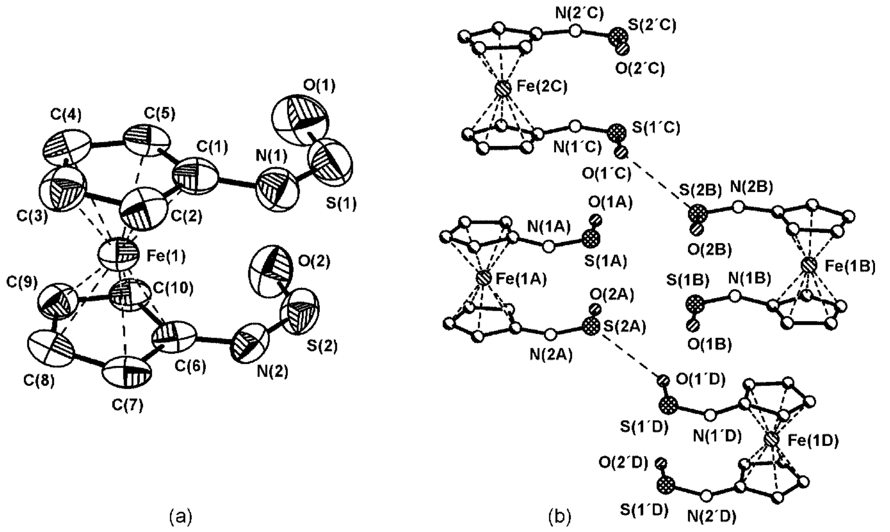


Figure 3. (a) Molecular structure of **5** (ORTEP plot, 50% probability; hydrogen atoms are omitted for clarity). S(1A)···S(2A) = 328.4, S(1′C)···S(2′C) 325.9 pm. For other selected distances and angles see Table 2. (b) Positions of the molecules of **5** in the lattice showing close intermolecular contacts: S(2A)···O(1′D) = 327.0, S(2B)···O(1′C) = 327.0 pm.

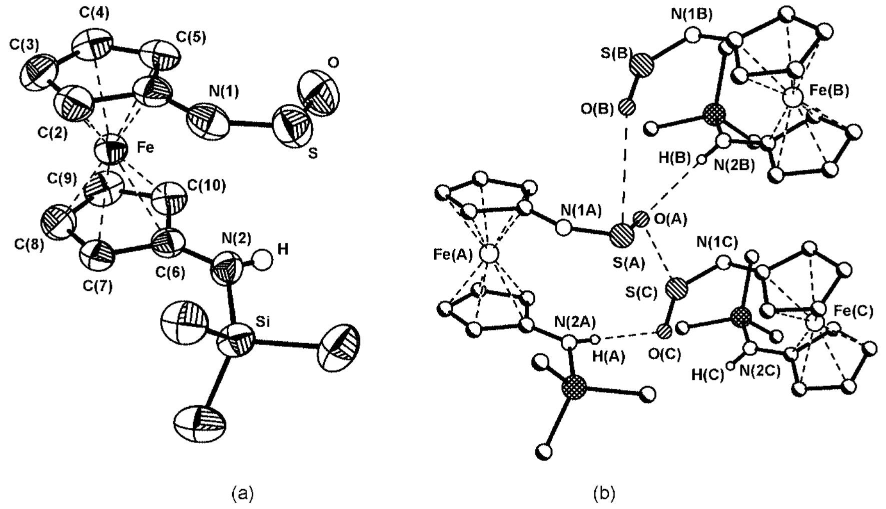


Figure 4. (a) Molecular structure of **8** (ORTEP plot, 50% probability; hydrogen atoms are omitted for clarity). For selected distances and angles see Table 2. (b) Positions of the molecules of **8** in the lattice showing close intermolecular contacts: O···H–N = 229.1, S···O = 328.9 pm.

eters are given in Table 2. In both cases, intermolecular interactions have to be considered, namely S···O contacts in **5** (Figure 3, b) and N–H···O bridges in **8** (Figure 4, b). It is tempting to trace the identical orientations of both NSO groups in **5** primarily to intermolecular interactions. However, there may also be important intramolecular contacts between the NSO groups, as indicated, for example, by the S···S contact (328.4 pm). The C–N vectors are slightly bent toward the iron atom (*β* = 4.1° and 5.7°[19]), and the C_5 rings are almost exactly in eclipsed positions (*τ* = 0.1° and 0.4°[19]). The bond lengths and angles of **5** are in the usual range and compare favourably with those found for **1**.[3]

In the case of **8**, the C–N(SO) vector points toward iron (5.0°), whereas the C–N(Si) vector points away from iron

Table 2. Selected bond lengths [pm] and angles [°][a] of the ferrocenes **1**,[b] **5** (Figure 3) and **8** (Figure 4).

1[c]		**5**		**8**	
C(1)–N(1)	140.02(2)	C(1)–N(1)	139.2(8)	C(1)–N(1)	139.0(4)
C(11)–N(2)	139.4(2)	C(1′)–N(1′)	138.0(8)		
–		C(6)–N(2)	138.8(8)	C(6)–N(2)	137.9(4)
		C(6′)–N(2′)	140.0(9)		
N(1)–S(1)	152.0(1)	N(1)–S(1)	152.8(6)	N(1)–S	151.2(3)
N(2)–S(2)	152.1(1)	N(1′)–S(1′)	152.3(6)		
–		N(2)–S(2)	151.9(6)	N(2)–Si	174.2(2)
		N(2′)–S(2′)	152.4(6)		
S(1)–O(1)	145.7(2)	S(1)–O(1)	144.4(6)	S–O	146.6(3)
S(2)–O(2)	146.6(2)	S(1′)–O(1′)	145.2(5)		
		S(2)–O(2)	144.6(6)	–	
		S(2′)–O(2′)	144.5(5)		
		H(5)···O(1)	256.8	H(5)···O	256.7
		H(5′)···O(1′)	249.4		
		H(10)···O(2)	253.7	–	
		H(10′)···O(2′)	247.6		
Fe(1)C_5(1)	164.5	Fe(1)C_5(1)	166.4	FeC_5(1)	164.9
Fe(2)C_5(1′)	164.6	Fe(2)C_5(1′)	165.9		
Fe(1)C_5(2)	165.4	Fe(1)C_5(2)	165.9	FeC_5(2)	166.6
Fe(2)C_5(2′)	165.6	Fe(2)C_5(2′)	166.2		
C_5/C_5 (α)	1.6	C_5/C_5 (α)	3.4	C_5/C_5 (α)	2.0
C_5/C_5 (α')	2.0	C_5/C_5 (α')	2.6		
C_5/N(1) (β_1)	< 1	C_5/N(1) (β_1)	4.7 (towards Fe)	C_5/N(1) (β_1)	5.0 (towards Fe)
C_5/N(1′) (β_1)	< 1	C_5/N(1′) (β_1)	5.3 (towards Fe)		
		C_5/N(2) (β_2)	5.0 (towards Fe)	C_5/N(2) (β_2)	2.9 (away from Fe)
		C_5/N(2′) (β_2)	3.9 (towards Fe)		
C_5–Fe(1)–C_5 (γ)	179.3	C_5–Fe(1)–C_5 (γ)	176.4	C_5–Fe–C_5 (γ)	178.8
C_5–Fe(2)–C_5 (γ')	178.1	C_5–Fe(2)–C_5 (γ')	176.8		
C_5/C_5 (twist) (τ)	2.0	C_5/C_5 (twist) (τ)	0.1	C_5/C_5(twist) (τ)	2.2
C_5/C_5 (twist) (τ')	2.5	C_5/C_5 (twist) (τ')	0.4		

[a] See ref.[19] for the definition of the angles *α*, *β*, *γ* and *τ*. [b] Taken from ref.[3]. [c] Data for two different molecules in the unit cell, as given in ref.[3]

(2.9°). The deviation from the eclipsed position of the cyclopentadienyl rings is again small (τ = 2.2°). Otherwise, the positions of the SO and the $SiMe_3$ groups are ideal for minimising steric interactions. The surroundings of the amino nitrogen atoms are close to trigonal planar.

Experimental Section

General: All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The deuterated solvents CD_2Cl_2 and $CDCl_3$ were distilled from CaH_2 under argon. All other solvents were distilled from Na metal in an atmosphere of argon. The starting materials 1,1′-diaminoferrocene (**2**),[6] 1,1′-bis(trimethylsilylamino)ferrocene (**3**)[6] and *N*,*N*′-dilithio-1,1′-bis(trimethylsilylamino)ferrocene (**4**) and [fc($NSiMe_3$)$_2$$Li_2$][7] were prepared as described in the literature. Triethylamine was distilled from Na prior to use. DMF was purchased from Aldrich and distilled from KOH. Other starting materials were purchased from Aldrich [butyllithium (1.6 M in hexane)] or Acros ($SOCl_2$, KO*t*Bu), and used without further purification. NMR measurements: Bruker ARX 250: ^{1}H, ^{13}C, ^{14}N, ^{15}N and ^{29}Si NMR (refocused INEPT[20] based on $^{2}J_{^{29}\mathrm{Si},^{1}\mathrm{H}}$ = 7 Hz); Bruker DRX 500: ^{57}Fe NMR; Varian INOVA 400: ^{1}H, ^{13}C NMR; chemical shifts are given with respect to Me_4Si [δ^{1}H ($CHDCl_2$) = 5.33 ppm; δ^{13}C (CD_2Cl_2) = 53.5 ppm; δ^{29}Si = 0 ppm for Ξ(^{29}Si) = 19.867184 MHz]; δ^{14}N = 0 ppm [external neat $MeNO_2$ with Ξ(^{14}N) = 7.226324 MHz], δ^{15}N = 0 ppm [external neat $MeNO_2$ with Ξ(^{15}N) = 10.136767 MHz]; δ^{57}Fe = 0 ppm [external neat $Fe(CO)_5$ with Ξ(^{57}Fe) = 3.237798 MHz]. IR spectra: Perkin–Elmer Spectrum 2000 FTIR. EI-mass spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70eV) with direct inlet; the *m*/*z* data refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{32}S, ^{28}Si, and ^{56}Fe. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

1,1′-Bis(sulfinylamino)ferrocene (5): A suspension of 1,1′-diaminoferrocene (**2**; 295 mg, 1.37 mmol) in Et_2O (20 mL) and triethylamine (0.91 mL, 6.52 mmol) was prepared. The suspension was cooled to –78 °C and $SOCl_2$ (326 mg, 0.20 mL, 2.74 mmol) dissolved in Et_2O (3 mL) was injected slowly with a syringe. The reaction mixture was stirred at –78 °C for 1 h; then it was allowed to reach ambient temperature and kept stirring for 1.5 h. Insoluble materials were filtered off, washed with Et_2O (20 mL), and volatile materials were removed from the filtrate in vacuo. The remaining violet-blue solid was dissolved in Et_2O (30 mL) and the violet solution was filtered. After removal of the solvent in vacuo the product **5** (220 mg; 52%) was left as a violet-blue solid. Crystallisation from CD_2Cl_2, after 2 weeks at –20 °C, gave violet crystals of **5** (m.p. 149–151 °C). ^{1}H NMR (250.1 MHz, CD_2Cl_2, 298 K): δ = 4.60 (m, 4 H, H$^{3,4,3',4'}$), 4.90 ppm (m, 4 H, H$^{2,5,2',5'}$). ^{1}H NMR (250.1 MHz, CD_2Cl_2, 203 K): δ = 4.63 (m, 4 H, H$^{3,4,3',4'}$), 4.55 ppm (br. m, 4 H, H$^{2,5,2',5'}$). EI-MS (70 eV) for $C_{10}H_8FeN_2O_2S_2$ (308.15): *m*/*z* (%) = 308 (100) [M^{+}], 244 (6) [M^{+} – SO_2], 212 (85) [M^{+} – 2SO], 182 (12), 166 (7), 134 (40), 116 (16), 108 (14), 82 (16), 56 [Fe^{+}] (74). IR (toluene) $\tilde{\nu}$ = 1261 cm^{-1} (ν_{as}), 1093 (ν_{s}) (NSO).

6-Amino-1-(sulfinylamino)ferrocene (6). Method A: The same procedure was employed as for **5**, except that an equimolar amount of $SOCl_2$ (175 mg, 1.48 mmol) in Et_2O (4 mL) was used and the reaction mixture was kept stirring for 20 h. A mixture was obtained (72 mg) which, according to NMR spectra, contained **6** (ca. 35%) and **5** (ca. 15%), together with a lot of **2** (ca. 50%), as a violet-blue solid. This solid was dissolved in hexane (20 mL) and the blue solution was filtered. After removing the solvent in vacuo **6** was left as blue solid which still contained some **5** (5%). Crystallisation from hexane at –30 °C, gave a blue powder of **6** (m.p. 79–81 °C).

Method B: Freshly distilled DMF (20 mL) was added to a mixture of **5** (38 mg; 0.12 mmol) and KO*t*Bu (15 mg; 0.13 mmol). The colour of the violet solution changed to blue. The reaction mixture was stirred for 1 h, and volatile materials were removed in vacuo. The remaining blue solid was dissolved in Et_2O (20 mL) and the blue solution was filtered. After removing the solvent in vacuo **6** (28 mg; 88%) was left as a blue solid. ^{1}H NMR (250.1 MHz, CD_2Cl_2, 298 K): δ = 2.75 (br. s, 2 H, NH), 3.82 (m, 2 H, H^{7,10}), 3.87 (m, 2 H, H^{8,9}), 4.54 (m, 2 H, H^{3,4}), 4.84 ppm (m, 2 H, H^{2,5}). ^{1}H NMR (250.1 MHz, CD_2Cl_2, 198 K): δ = 2.95 (br. s, 2 H, NH), 3.58 (m, 2 H, H^{7,10}), 3.78, 3.87 (m, m, 1 H, 1 H, H^{8,9}), 4.10, 5.03 (m, m, 1 H, 1 H, H^{2,5}), 4.51 ppm (m, 2 H, H^{3,4}). EI-MS (70 eV) for $C_{10}H_{10}FeN_2OS$ (262.11): *m*/*z* (%) = 262 (100) [M^{+}], 214 (12) [M^{+} – SO], 198 (12) [M^{+} – SO – NH_2], 197 (11), 187 (12), 185 (6), 152 (6), 137 (13), 135 (16), 133 (18), 108 (6), 80 [$CpNH_2^{+}$] (56), 56 [Fe^{+}] (31). IR (toluene) $\tilde{\nu}$ = 1261 cm^{-1} (ν_{as}), 1097 (ν_{s}) (NSO).

1-(Sulfinylamino)-6-(trimethylsilylamino)ferrocene (8): A solution of 1,1′-bis(trimethylsilylamino)ferrocene (**3**; 240 mg, 0.67 mmol) in Et_2O (20 mL) and triethylamine (0.19 mL, 1.36 mmol) was prepared. The solution was cooled to –78 °C, and $SOCl_2$ (79 mg, 0.049 mL, 0.67 mmol) dissolved in Et_2O (4 mL) was injected slowly with a syringe. The reaction mixture was stirred at –78 °C for 1 h, then it was allowed to reach ambient temperature and kept stirring for 20 h. Insoluble materials were filtered off, and volatiles were removed from the filtrate in vacuo to give 185 mg of a mixture containing **8** (ca. 90%) and **5** (ca. 10%) as a blue solid. This solid was dissolved in hexane (20 mL) and the blue solution was filtered. After removing the solvent in vacuo **8** was left as a blue solid. Crystallisation from hexane/CH_2Cl_2 (1:1), after 2 weeks at –30 °C, gave blue crystals of **8** (m.p. 89–91 °C). ^{1}H NMR (250.1 MHz, CD_2Cl_2, 298 K): δ = 0.20 (s, 9 H, Me_3Si), 2.30 (br. s, 1 H, NH), 3.75 (m, 2 H, H^{7,10}), 3.88 (m, 2 H, H^{8,9}), 4.53 (m, 2 H, H^{3,4}), 4.79 ppm (m, 2 H, H^{2,5}). ^{1}H NMR (250.1 MHz, CD_2Cl_2, 203 K): δ = 0.08 (s, 9 H, Me_3Si), 2.60 (br. s, 1 H, NH), 3.45, 3.59 (m, m, 1 H, 1 H, H^{7,10}), 3.75, 3.89 (m, m, 1 H, 1 H, H^{8,9}), 4.04, 5.06 (m, m, 1 H, 1 H, H^{2,5}), 4.51, 4.53 ppm (m, m, 1 H, 1 H, H^{3,4}). EI-MS (70 eV) for $C_{13}H_{18}FeN_2OSSi$ (334.29): *m*/*z* (%) = 334 (100) [M^{+}], 286 (6) [M^{+} – SO], 271 (10) [M^{+} – CH_3SO], 234 (9), 205 (13), 182 (7) [FeCpNSO^{+}], 178 (6), 152 (20) [CpN(H)$SiMe_3^{+}$], 134 (22) [FeCpN^{+}], 108 (6), 73 [$SiMe_3^{+}$] (71), 56 [Fe^{+}] (13). IR (toluene) $\tilde{\nu}$ = 1261 cm^{-1} (ν_{as}), 1096 (ν_{s}) (NSO).

1,3-Bis(trimethylsilyl)-2-oxo-1,3,2-diazathia-[3]ferrocenophane (9): Freshly prepared fc($NSiMe_3$)$_2$$Li_2$ (**4**; 300 mg, 0.83 mmol) was dissolved in Et_2O (20 mL), the solution was cooled to –78 °C, and $SOCl_2$ (55 mg, 0.034 mL, 0.46 mmol) dissolved in Et_2O (4 mL) was injected slowly with a syringe. The reaction mixture was stirred at –78 °C for 0.5 h, then it was allowed to reach ambient temperature and kept stirring for 20 h. Volatile materials were removed in vacuo, and the resulting oil was dissolved in hexane (20 mL). Insoluble materials were separated by centrifugation, and the clear liquid was collected. The solvent was removed in vacuo to give 204 mg of a mixture containing **9** (ca. 25%) and **3** (ca. 75%) as a green oil. ^{1}H NMR (250.1 MHz, CD_2Cl_2, 298 K): δ = 0.26 (s, 18 H, Me_3Si), 3.82, 3.86 (m, m, 2 H, 2 H, H$^{2,3,2',3'}$), 4.13, 4.19 (m, m, 2 H, 2 H, H$^{4,5,4',5'}$).

Crystal Structure Determinations of the Ferrocenes 5 and 8: Details pertinent to the crystal structure determinations are listed in

Table 3. Crystallographic data for the ferrocenes **5** and **8**.

	5	**8**
Formula	$C_{10}H_8FeN_2O_2S_2$	$C_{13}H_{18}FeN_2OSSi$
Crystal	violet prism	blue needle
Dimensions [mm]	0.20 × 0.18 × 0.16	0.28 × 0.18 × 0.16
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Lattice parameters (pm [°])	a = 1041.8(2) b = 1091.9(2) c = 1113.6(2) α = 63.68(3) β = 86.44(3) γ = 79.73(3)	a = 878.21(18) b = 697.96(14) c = 2455.6(5) β = 92.75(3)
Z	2	4
Absorption coefficient μ [mm^{-1}]	1.711	1.214
Diffractometer	STOE IPDS I (Mo-K_α, λ = 71.073 pm), graphite monochromator	
Measuring range (ϑ [°])	2.0–26	2.4–25.9
Reflections collected	7630	2743
Independent reflections [$I > 2\sigma[I]$]	3998	2743
Absorption correction[a]	none	numerical
Refined parameters	307	175
wR_2/R_1 [$I > 2\sigma[I]$]	0.122/0.054	0.085/0.036
Max./min. residual electron density (10^{-6} e pm^{-3})	0.597/–0.375	0.626/–0.210

[a] Absorption corrections did not improve the parameter set.

Table 3. Crystals of appropriate size were sealed under argon in a Lindemann capillary, and the data collections were carried out at 20 °C.[21]

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[21] CCDC-600889 (for **5**) and -600888 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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