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Ferrocenes with a Persulfurated Cyclopentadienyl Ring: Synthesis, Structural Studies, and Optoelectronic Properties

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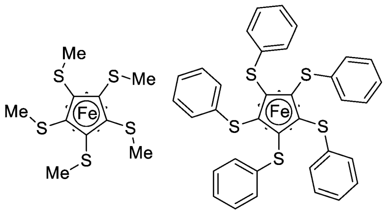
Abstract: Persulfurated arenes are a fascinating class of functional molecules with a wide range of potential applications. Ferrocenes are also a multifaceted class of aromatic compounds that can easily be finetuned for an enormous variety of desired properties. A combination of both substance classes might yield an even wider field of applications. Herein, we describe the synthesis of two ferrocenes with one persulfurated cyclopentadienyl ring $[C_5(SR)_5]$, with R = Me or Ph, together with their crystal structures, optical, and electrochemical properties. Both crystal structures show significant intramolecular sulfur-iron interactions as well as weak intermolecular sulfur–contacts. Cyclovoltammetry of the $[C_5(SPh)_5]$ compound shows a high oxidation potential of 651 mV vs. FcH/FcH$^+$.

Persulfurated arenes still remain an underexploited field of chemistry, despite their highly interesting physical organic properties and their numerous possible applications, ranging from ion-selective membranes over organic conductors and ferromagnets to cation sensors and liquid crystals.[1] This statement made by M. Gingras in a fascinating review article in this journal more than 10 years ago is still valid. There have been, however, several interesting additions to this field, particularly with extended aromatic systems. Per(arylthio)corannulenes and -coronenes have found potential application as photovoltaic devices[2] and for molecular electronics.[3] Substituted hexakis(phenylthio)benzenes showed strong phosphorescence in the solid state with the potential of OLED applications.[4] Dendrimers with a $[C_6(SAr)_6]$ core, so-called "molecular asterisks" have been used as multifunctional ligands for the preparation of luminescent sensors and asymmetric metal catalysis.[5] The interesting electronic properties shared by this compound class are mainly due to the fact that "phenylthio substituents attached to aromatic cores result in a reduction of the HOMO–LUMO gap",[1,2a] "primarily due to LUMO stabilization".[6] Upon addition of SPh groups a bathochromic shift of the longest wavelength absorption by 10–15 nm is observed together with an increase of the reduction potential by 0.1 V.[2b]

Metallocenes are another very important group of aromatics with very interesting electronic properties. However, while quite a few metal-free persulfurated arenes have been studied, there seem to be no reports of persulfurated ferrocenes. The fivefold symmetry of metallocenes would create a structural motif rarely found with thioether-based "molecular asterisks" (Scheme 1).[7]



Scheme 1. Molecular asterisks based on ferrocene.

While the syntheses of persulfurated cyclopentadienyl anions $[C_5(SR)_5]^-$ (R = Me, Ph) was already reported in the 1980s,[8] attempts to prepare metallocenes from them via reactions with metal halides met with failure. However, the complexes $[C_5(SMe)_5]ML_n$ (ML_n = $Mn(CO)_3$, RuCp*) could be obtained via post-functionalization of an already coordinated cyclopentadienyl ring.[9,10] Transfer of this synthetic protocol using perhalogenated or permercurated ferrocenes was not successful.[11,12] This failure was attributed to a competing lithium–thiolate exchange instead of the desired lithium–halide exchange. "Bottom-up approaches", that is, successive introduction of SR groups starting from ferrocene or $[C_5H_4(SR)]Fe[C_5H_5]$, were apparently not attempted, except for the preparation of 1,1′,2,2′-tetrakis(methylthio)ferrocene.[13]

Inspired by two publications on bromide/halide-mediated *ortho*-deprotonations for the synthesis of di- and trisubstituted ferrocenes,[14] we reasoned that the synthetic approach depicted in Scheme 1 might lead to the desired $[C_5(SR)_5]$ complexes. The first step resembles a synthetic procedure described for the synthesis of other 2-substituted bromoferrocenes,[14b,15] whereas the second step corresponds to a procedure used for the synthesis of $[C_5(STol\text{-}p)(Br)(CHO)H_2]Fe[C_5H_5]$ with

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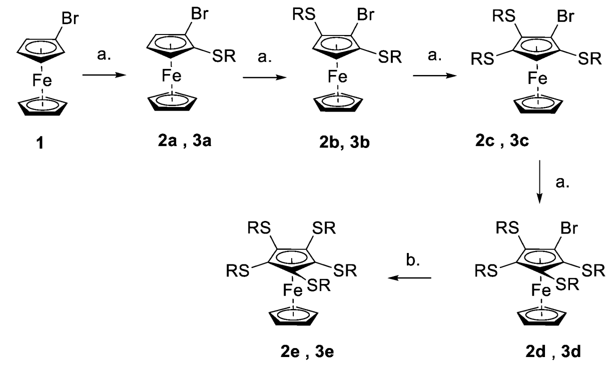

Scheme 2. Preparation of $[C_5(SR)_5]Fe[C_5H_5]$, R = Me (**2e**), Ph (**3e**): a) 1. LiTMP, 2. S_2R_2, solvent THF; b) 1. *n*BuLi, 2. S_2R_2, solvent Et_2O.

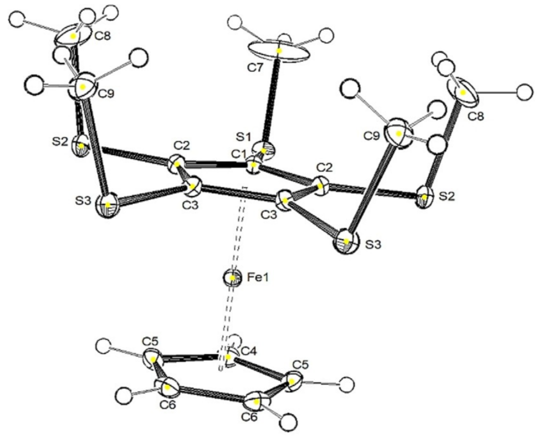

Figure 1. Molecular structure of **2e** in the crystal. Thermal ellipsoids are drawn at the 30 % probability level.

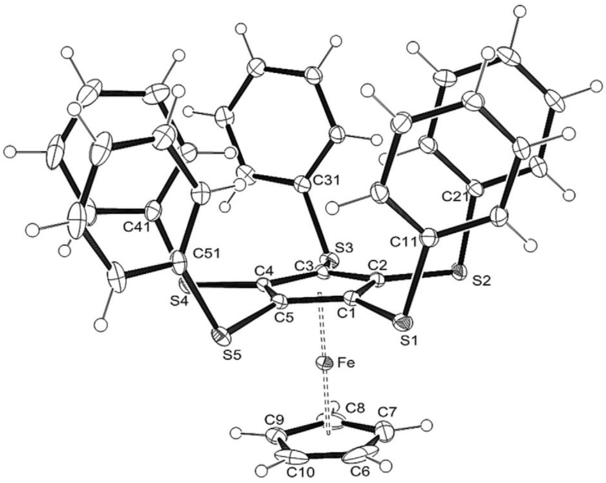

Figure 2. Molecular structure of **3e** in the crystal. Thermal ellipsoids are drawn at the 30 % probability level.

the intention of preparing 1,3-difunctionalized ferrocenes (Scheme 2).[14a]

As already observed for the latter case, also here only the products **2b** (R = Me) and **3b** (R = Ph) of deprotonation next to the bromo substituent are obtained. All deprotonations were carried out at −30 °C. For the syntheses of **2a**–**d** and **3a**–**d** the solutions were cooled down to −78 °C and treated with the disulfide and the reaction mixtures were slowly warmed to room temperature afterwards. For the Br–Li exchange reaction the solution of **2d** was cooled down to −90 °C, treated with *n*-butyl lithium and then with S_2Me_2, whereas the solution of **3d** was cooled to −78 °C, treated with *n*-butyl lithium and then with S_2Ph_2. Compound **2e** was isolated as an orange solid in an overall yield of 4.4 %, whereas **3e** was obtained as a yellow solid in an overall yield of 6.2 %. When compounds **2a** and **3a**–**c** were treated with *n*-butyl lithium instead of lithium tetramethylpiperidinide, followed by addition of disulfides S_2R_2, the bromine-free ferrocenyl thioethers $[C_5(SR)_{5-n}H_n]Fe[C_5H_5]$ (R = Me, $n = 3$: **2b″**, R = Ph, $n = 3$–5: **3b′**--**3d′**) were obtained in good to excellent yields. All compounds were characterized by ^1H and ^{13}C NMR and (HR)MS spectra (see the Supporting Information).

Recrystallization of **2e** and **3e** from diethylether gave yellow platelets and blocks, respectively, which were suitable for crystal structure determinations. Compound **2e** crystallized in the orthorhombic space group *Pnma*, whereas **3e** crystallized in the monoclinic space group $P2_1/c$. Further experimental details of the structure determinations can be found in Table S1 of the Supporting Information. ORTEP representations of both structures are depicted in Figures 1 and 2.

The asymmetric unit of **2e** contains only half a molecule with the iron atom, the sulfur atom S1 and carbon atoms C1, C4 and C7 on a mirror plane. Both cyclopentadienyl rings are close to parallel and in an exactly eclipsed conformation, which is in part due to symmetry requirements. As can be seen in Figure 1, the "real" molecule slightly deviates from this crystallographic requirement, which shows up in the oblate form of the thermal ellipsoid of the methyl carbon atom C7. The substituted cyclopentadienyl ring is about 0.04 Å closer to the iron atom than the unsubstituted ring, and all sulfur atoms are on the proximal side of the ring. The iron–sulfur distances are in the range 3.3293(1) to 3.3744(1) Å and thus significantly shorter than the sum of van der Waals radii (3.94 Å).

Both cyclopentadienyl rings are highly regular pentagons, with the bond lengths within the substituted ring being approximately 0.02 Å longer than in the unsubstituted one. The methyl groups are all in an axial position at sulfur on the distal side of the ring, with C-C-S-C torsion angles of 93 ± 9°. This unexpected orientation of the methyl group differs from the one observed in the manganese complex $[C_5(SMe)_5]Mn(CO)_3$, in which two methyl groups are situated on the same side of the ring as the manganese atom.[6] According to a theoretical study on the structure of $C_6(SMe)_6$ an "ababab" conformation with alternating positions of the methyl groups above and below the ring plane is the energy minimum.[16] As pentagons do not allow for a stringent alternance of "above" and "below" positions, the conformation of the manganese complex comes very close to the calculated $[C_6(SMe)_6]$ minimum. In the structure of the above-mentioned uncomplexed $[C_5(SMe)_5]$ salt (with a $AsPh_4$ cation) an "aaaab" conformation is observed.[8a] The conformation observed in **2e** corresponds to an energy maximum in the benzene case, which is of course only partially comparable due to the different point symmetries and also the sterical influence of the CpFe group in **2e**.

When looking at intermolecular interactions, one can identify weak S–S interactions between S2 and S3, which link always four molecular units to a macrocycle, and these macrocycles are connected along the (0 1 1) direction to an infinite ribbon (see Figure S12 of the Supporting Information). The crystals of **2e** contain 3.0% solvent accessible voids, which are lined up along the crystallographic *c*-direction (see Figure S13, Supporting Information)

In the crystal of **3e** the asymmetric unit consists of a whole molecule. Both rings are exactly parallel and nearly ideally eclipsed. The substituted ring is an ideal pentagon with C–C bonds of 1.4425 ± 0.0015 Å and its centroid 1.662 Å away from the iron. The unsubstituted ring shows strong librational effects and an unresolved disorder towards eclipsed-staggered conformation with its centroid 1.613 Å away from iron. As was already observed in the structure of **2e**, the sulfur atoms are all situated on the proximal side of the cyclopentadienyl ring with distances to the iron atom ranging from 3.2530(7) to 3.3682(7) Å, again significantly shorter than the sum of the van der Waals radii and also slightly shorter than in **2e**. Also similarly to **2e**, the phenyl rings are all in axial positions on the distal side of the cyclopentadienyl ring, with C-C-S-C torsion angles ranging from approximately 75.0 to 95°. The orientations of the phenyl rings relative to the cyclopentadienyl ring are quite different from each other, with ψ angles[17] ranging from approximately 45 to approximately 180°. In the crystal structures of [$C_6(SPh)_6$] and some *para*-substituted derivatives again an "ababab" conformation is observed,[4a,17] although DFT calculations showed that an "abbabb" conformation would be energetically favorable.[4b]

In contrast to the structure of **2e** there are no weak S–S interactions in **3e** (see Figure S14, Supporting Information), but there are also solvent accessible voids which make up for 3.2% of the cell volume, and which are again lined up along the crystallographic *c*-direction. (see Figure S15, Supporting Information)

UV/Vis spectra of dichloromethane solutions show for both compounds the typical "ferrocene band" at 437 ± 1 ($\varepsilon = 160$, **2e**) and 439 ± 2 nm ($\varepsilon = 194$, **3e**) (see Figures 3 and Figures S6/S7). Compounds **2e** and **3e** also show strong bands at 265/295 nm and 250 nm, respectively. For comparison, the literature values for both ferrocene and [$C_5H_4(SPh)$]Fe[C_5H_5] are 325 and 440 nm.[18,19] The so-called "optical band gap", defined either from the long-wave absorption maxima or from the onsets of these bands,[20,21] can thus be calculated as 2.82–2.84 or 2.37–2.38 eV, respectively. This lack of sensitivity towards substituent effects is in sharp contrast to the above-mentioned observation with metal-free persulfurated arenes,[1,2a,22] but confirms the old observation for ferrocenes that this band is "relatively insensitive to substitution on the ring".[23] Also not very astonishing, both compounds showed neither fluorescence nor phosphorescence.

Next, we turned to the electrochemical properties and performed a cyclovoltammetry experiment (Figure 4). There have been many studies on the relationship between ionization and oxidation potentials, in general[20b,24] and especially for ferrocene,[25] as well as on the computation of absolute HOMO and LUMO levels from the electrochemical band gap.[26]

Both compounds show one reversible oxidation peak with $E_{1/2} = 0.343$ for **2e** and 0.651 V for **3e**, relative to the internal

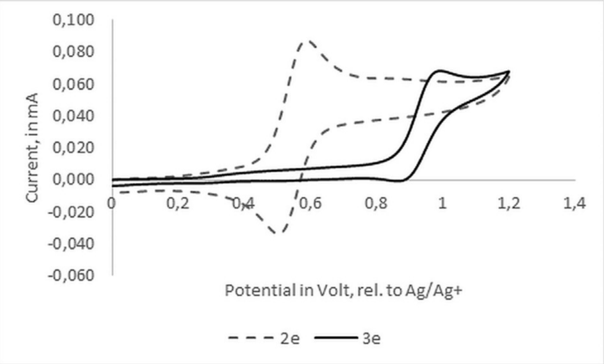

Figure 4. Cyclovoltammogram of **2e** and **3e**.

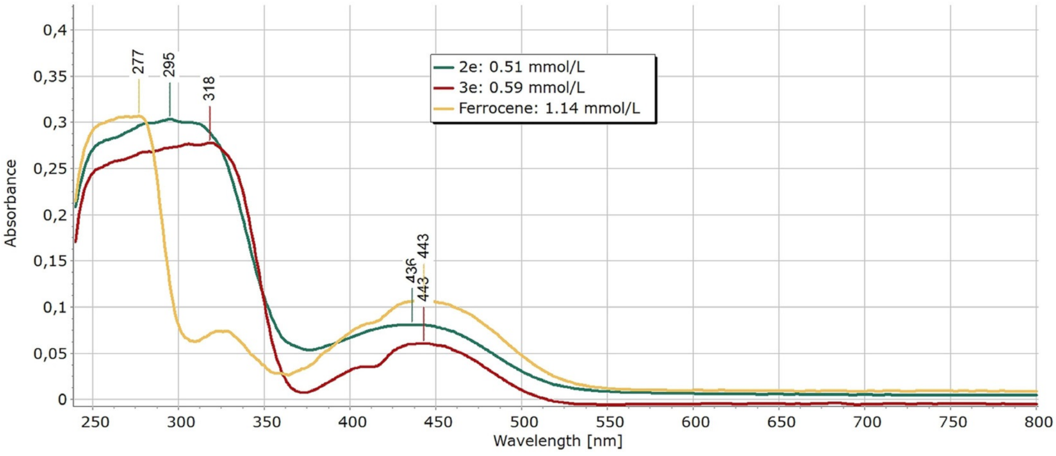

Figure 3. UV/Vis spectra of **2e** and **3e** and ferrocene as solutions in CH_2Cl_2.

Table 1. Oxidation potentials (vs. Fc/Fc$^+$) of **2e**, **3e** and some related compounds.

Compound	$E_{1/2}$ [V]	Ref.
2e	0.343	this work
3e	0.651	this work
FcSPh	0.059	–[15]
	0.130	–[27]
FcSeMe	0.025	–[28]
$[C_5H_4(SMe)]_2Fe$	−0.025	–[29]
$[C_5H_3(SMe)_2]_2Fe$	0.00	–[10]
$FcSMe_2{}^+TFSI^-$	0.530	–[30]

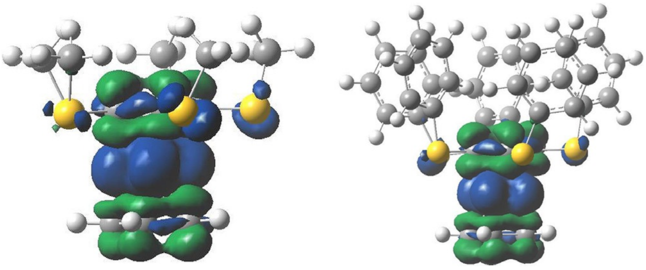

Figure 5. Spin densities of frozen one-electron-oxidized states of **2e** (left) and **3e**, calculated at the (U)B3LYP-D3/Def2SVP level of theory.

FcH/FcH$^+$ couple (see also Figures S1 and S2). The oxidation potentials of **2e**, **3e**, and some related Ferrocenyl chalcogeno ethers are collected in Table 1. Using the (second) reported value for FcSPh, that is, 0.130 V, the measured value for **3e** fits nicely to the "substituent additivity rule" value of 5×0.130 V. The fact that the oxidation potential of **3e** is significantly higher than that of **2e** is unexpected, as phenylthio substituents are known to better stabilize a radical cation than a methylthio substituent, and therefore it can be concluded that the oxidation must take place at the iron center. We also tried to measure the reduction wave of both compounds and performed scans from −2.2 eV to +1.2 V (vs. Ag/Ag$^+$, see Figures S3–S5, Supporting Information). Both compounds show irreversible reduction waves, however, for **2e** a cathodic peak around −1.9 V might be associated with the reduction of **2e**. Again, this finding is rather unexpected, as most persulfurated arenes can easily be reduced due to the radical-anion stabilizing effect of the thioether substituents.[6] It seems therefore possible, that upon reduction the persulfurated cyclopentadienyl ligand is lost from the ferrocene, and the observed reduction waves occur on the "free" ligands.

The rather high oxidation potential of **3e** (there are, however, quite a few ferrocene derivatives with electron-withdrawing substituents on both rings which are much more difficult to oxidize) makes it difficult to find an appropriate chemical oxidizer, and all our attempts to this end met with failure. The question, if the electrochemical oxidation takes place at the iron center or the sulfur atoms (which is at least possible for FcSMe[31]), was therefore also addressed by DFT calculations. The geometry optimizations have been performed at the B3LYP-D3/Def2SVP level of theory in the gas phase.[32] Thermochemical corrections to 298.15 K were calculated at the same level of theory using the rigid rotor/ harmonic oscillator model. The enthalpy (ΔH_{298}) at the B3LYP-D3/Def2SVP level was obtained through the addition of the corresponding ΔH to ΔE_{tot}, respectively. For both, **2e** and **3e**, the singlet electronic state is the most stable configuration (see Figure S16, Supporting Information). For **2e** the iron center has the biggest contribution to the HOMO indicating that the electron most probably will be removed from the metal, whereas in the case of **3e** the HOMO is mainly located at the aromatic π-system making the formation of a radical at the sulfur atom more likely (see Figure S18, Supporting Information). Spin density calculations show, however, that the unpaired electron on the frozen one-electron oxidized species is located at the $FeCp_2$ moiety for both molecules (Figure 5).

Our calculations yield HOMO energies for FcH, **2e**, and **3e** of −5.39, −5.75, and −5.74 eV, respectively (see Figure S17, Supporting Information). The introduction of the thioether groups thus leads to a reduction of the HOMO–LUMO-gap from 5.27 eV in ferrocene to 5.16 eV for **2e** and to 4.81 eV for **3e** (i.e. 0.46 eV or 5×0.092 eV). This reduction is slightly smaller than for the literature-known compounds in the benzene series (0.1 eV/SPh). The common practice of associating the HOMO–LUMO gap with the "optical band gap" (see above) clearly cannot applied here, and, therefore, once again, one should always keep in mind that spectra "measure differences in state energies, not orbital energies".[21d,e]

Using the presumed relationship between E_{ox} and ionization potential or HOMO position,[24] and assuming the reported value for the absolute potential of ferrocene as 5.39 eV, [26b] we obtain for the HOMO of **2e** a value of −5.733 eV and for **3e** a value of −6.04 eV. This gives a nice agreement with our calculations for **2e**, but a rather large deviation of 0.30 eV for **3e**. It appears, therefore, possible that in the electrochemical experiment, ionization of **3e** does not occur from the HOMO, but from one of the lower-lying orbitals.

In conclusion, we can state that the synthesis of ferrocenes with one persulfurated cyclopentadienyl ring with both aliphatic and aromatic residues could be achieved in a five-step procedure starting from bromoferrocene. As long as the corresponding disulfides are available, this synthetic protocol should also work for other alkyl and aryl thiolate substituents. As the electrochemical properties are quite different from ferrocene and from metal-free persulfurated aromatic compounds, the compounds described here might comprise a new substance class. The UV/Vis spectra and the optical properties of the persulfurated ferrocenes in general don't change in comparison with the parent compound, and therefore applications in the field of optical devices are rather unlikely.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: electrochemistry · metalation · metallocenes · persulfurated arenes · X-ray diffraction

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