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. 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(arylmethythio)corannulenes and -coronenes have found potential application as photovoltaic devices and for molecular electronics. Substituted hexakis(phenylthio)benzenes showed strong phosphorescence in the solid state with the potential of OLED applications. Den- trimers with a \([C_5(SR)_5]\) core, so-called “molecular asterisks” have been used as multifunctional ligands for the preparation of luminescent sensors and asymmetric metal catalysis. 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”.\(^{(3)}\) 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).\(^{(2)}\)

While the syntheses of persulfurated cyclopentadienyl anions \([C_5(SR)_5]^+\) (R = Me, Ph) was already reported in the 1980s,\(^{(2,3)}\) attempts to prepare metallocenes from them via reactions with metal halides met with failure. However, the complexes \([C_5(SMe)_5]Mn_5\) (Mn = Mn(CO)\(_5\), RuCp\(_2\)) could be obtained via post-functionalization of an already coordinated cyclopentadienyl ring.\(^{(5,6)}\) 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 \([C_5H_4(SR)]Fe[C_5H_5]n\) were apparently not attempted, except for the preparation of 1,1′,2,2′-tetakis(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 \([C_5(S Tol-p)(Br)(CHO)H]Fe[C_5H_5]n\) with

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**Scheme 1. Molecular asterisks based on ferrocene.**
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-butyllithium and then with S2Me2, whereas the solution of 3d was cooled to −78 °C, treated with n-butyllithium and then with S2Ph2. 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-butyllithium instead of lithium tetramethylpiperidinidide, followed by addition of disulfides S2R2, the bromine-free ferrocenyl thioethers [C6(SR)2]2Fe[CH3]2 (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 13C 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 P21/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 obtuse 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 [C6(SMe)2]2Mn(CO)5, in which two methyl groups are situated on the same side of the ring as the manganese atom.[9] According to a theoretical study on the structure of C6(SMe)2 an “aabab” 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 [C6(SMe)2] minimum. In the structure of the above-mentioned uncomplexed [C6(SMe)2] salt (with a AsPh4 cation) an “aaaaab” conformation is observed.[16]

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(15) 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 ranging from approximately 45 to approximately 180°. In the crystal structures of [C6(SPh)4]Fe[C5H5] and some para-substituted derivatives again an “ababab” conformation is observed, although DFT calculations showed that an “abbabb” conformation would be energetically favorable.

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).

Figure 3. UV/Vis spectra of 2e and 3e and ferrocene as solutions in CH2Cl2.

UV/Vis spectra of dichloromethane solutions show for both compounds the typical “ferrocene band” at 437 ± 1 (ε = 160, 2e) and 439 ± 2 nm (ε = 194, 3e) (see Figures S3 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 [C6H4(SPh)Fe[C5H5]] are 325 and 440 nm. The so-called “optical band gap”, defined either from the long-wave absorption maxima or from the onsets of these bands, 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, but confirms the old observation for ferrocenes that this band is “relatively insensitive to substitution on the ring”. Also not very astonishing, both compounds showed neither fluorescence nor phosphorescence.

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

Both compounds show one reversible oxidation peak with $E_{1/2} = 0.343$ V for 2e and 0.651 V for 3e, relative to the internal...
The oxidation potentials of 2e, 3e, and some related Ferrocenyl chalcogenoethers 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 methythio 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.[8] 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 FcSeMe[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.[23] Thermochanical corrections to 298.15 K were calculated at the same level of theory using the rigid rotor/ harmonic oscillator model. The enthalpy (ΔH̃) at the B3LYP-D3/Def2SVP level was obtained through the addition of the corresponding ΔH to ΔEcorr, 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 FeCp₂ 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.”[24,25]

Using the presumed relationship between Ecorr and ionization potential or HOMO position,[24] and assuming the reported value for the absolute potential of ferrocene as 5.39 eV,[26] 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 and 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 · metallocones · persulfurated arenes · X-ray diffraction

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