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Investigation into the Redox Behavior of $Cp^*{}_2Fe_2(\mu\text{-}\eta^1\text{-}S_2)(\mu\text{-}\eta^2\text{-}S_2)$ ($Cp^* = \eta^5\text{-}C_5Me_5$): An Unexpected Reversible $\eta^1 \rightleftharpoons \eta^2$ Rearrangement of a Disulfur Bridge

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Reaction of $Cp^*{}_2Fe_2(\mu\text{-}\eta^1\text{-}S_2)(\mu\text{-}\eta^2\text{-}S_2)$ with oxidizing agents, e.g. Br_2, I_2, and $(C_5H_5)_2Fe^+X^-$ ($X = PF_6$, BF_4), gives the dicationic complex $Cp^*{}_2Fe_2S_4{}^{2+}$ along with the corresponding counteranions. An X-ray structure investigation on $[Cp^*{}_2Fe_2S_4]I_2$ reveals that the originally η^1-bonded S_2 ligand has been converted into a η^2-S_2 bridge by a 90° rotation. As a consequence of enhanced stereochemical constraints, the Fe–Fe distance is reduced by 0.7 Å to 2.883 (3) Å during this reaction. As can be shown from cyclic voltammetry experiments, the oxidation occurs in two one-electron steps well separated from each other (0.25 and 1.24 V, CH_2Cl_2, SCE). The main pathway for this process is the disproportionation of the intermediate monocation $Cp^*{}_2Fe_2S_4{}^+$ (I^+), which appears to be assisted by nucleophilic agents, e.g. CH_3CN and I^-. It was impossible to synthesize I^+ in bulk quantities. With strong reducing agents, e.g. CH_3Li and Li_2S_2, $[Cp^*{}_2Fe_2S_4]I_2$ is reduced to $Cp^*{}_2Fe_2S_4$ in good yields. These results are evidence for an unprecedented reversible η^1-$S_2 \rightleftharpoons \eta^2$-$S_2$ rearrangement that is induced by electron-transfer processes.

Introduction

One of the principal goals in the chemistry of soluble transition-metal sulfides besides the systematic development of synthetic routes to new products is the examination of the reaction behavior of such compounds. In most cases the sulfur ligands turned out to be reactive electron-rich centers,[1–4] and only relatively few examples are known where the metal is a reactive center as well.[5] A wide potential including both reaction types has been found during the past few years in the rapidly growing class of sulfur-rich dimeric cyclopentadienyl transition-metal complexes of general composition $Cp_2M_2S_x$ ($x \geq 4$).[6] Particular representatives of this class of compounds are the dinuclear group VIII derivatives $(C_5R_5)_2M_2S_4$ (M = Fe, Ru; R = H (Cp), R = CH_3 (Cp*)), which are distinguished by a unique set of two disulfur ligands being perpendicularly oriented to each other.[3,7] Such a combination might be expected to exhibit an extensive redox chemistry as has been already found for the isoelectronic complex $Cp_2Fe_2(SEt)_2(S_2)$ (III),[8] which incorporates a planar Fe–S_2–Fe geometry as well.[9] The general importance of redox chemistry at iron–sulfur cores has been already stressed in recent publications.[10] In particular it seemed interesting to us to subject complexes of the above type to an electrophilic attack by halogens although it has been already established that η^2-X_2 (X = S, Se) units are eliminated in elemental form from mononuclear complexes by these reagents.[11] In this work we show that the disulfur ligands in I remain in the molecule upon halogen oxidation. They do not form, however, relatively unstable sulfur–iodine bonds[12] but they balance the altered electronic situation at the metal atoms by a reversible $\eta^1 \rightleftharpoons \eta^2$ rearrangement.

Experimental Section

General Remarks. All manipulations were carried out under nitrogen with N_2-saturated, dry solvents. $Cp^*{}_2Fe_2S_4$ (I), was prepared as described previously from $Cp^*{}_2Fe_2(CO)_4$ and excess sulfur in toluene solution at 100 °C.[7]

X-ray Data Collection and Structure Refinement. Suitable dark brown crystals of complex IIb of needle-shaped habit were obtained from a CH_2Cl_2 solution at −25 °C. Data for a crystal of approximate dimensions 0.03 × 0.02 × 0.4 mm were collected on a Siemens-Stoe AED II four-circle diffractometer at room temperature by using monochromatic Mo Kα radiation (λ = 0.71073 Å). Accurate unit-cell dimension and crystal orientation matrices were obtained from least-squares refinement of setting angles ($5.99° \leq 2\theta \leq 19.08°$) of 40 machine-centered reflections.

IIb crystallizes in the monoclinic space group C_{2h}^5-$P2_1/c$, with a = 8.334 (3) Å, b = 12.070 (4) Å, c = 16.570 (3) Å, β = 96.44 (2)°, V = 1656.3 Å^3, Z = 2, $F(000)$ = 912, and D(measd) = 1.87 g cm^{-3}. Lorentz and polarization corrections as well as an empirical absorption correction (ψ scans of seven reflections with $4.92° < 2\theta < 37.61°$, μ = 31.30 cm^{-1}, minimum transmission of 0.4683, and maxima of 0.6297) were applied. Data collection ($\theta/2\theta$ scans $2.5° \leq 2\theta \leq 60°$) yielded 2184 reflections with $I > 3.0\sigma(I)$ (2020 unique reflections, 1997 used for refinement, R_{merge} = 0.034). Two standard reflections were measured every 2 h, with no fluctuations being observed.

The structure was solved by using standard Patterson methods, least-squares refinement, and Fourier techniques. Final refinement was achieved by a cascaded block-matrix procedure based on F with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were included "riding" on calculated positions (C–H distances fixed at 0.6 Å), yielding R = 0.04, and R_w = 0.032 (weighting scheme $W = (1/\sigma)(F)^2$, GOF = 1.54, number of parameters to refine 154, maximum Δ/σ = 2.81, and mean 0.55, with the largest features in final difference Fourier map at +0.2 and −0.3 e/Å^3).

All calculations were performed with the STRUCSY 84 program;[13] scattering factors including anomalous dispersion were taken from ref 14.

Electrochemical Techniques. Acetonitrile (Merck Uvasol) was twice vacuum distilled from P_4O_{10} and once from CaH_2. Dichloromethane was refluxed over P_4O_{10} and fractionated. Tetrabutylammonium hexafluorophosphate was repeatedly recrystallized from aqueous ethanol and dried at 10^{-5} bar for 48 h. Cyclic voltammograms (CV) were measured under dry nitrogen at ambient temperature by using a three-electrode cell with a Pt-disk working electrode and a salt-bridged saturated calomel (SCE) reference electrode. Coulometry by exhaustive potential con-

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trolled electrolysis was performed in a vacuum-line H-cell. The working compartment was equipped with a 4 cm^2 Pt flag and a Ag/AgCl electrode as quasi-reference electrode. An additional Pt disk allowed for the taking of CV's whenever desired. Potentials were calibrated by addition of ferrocene (E_0' (SCE) = 0.42 V (CH_3CN) or 0.47 V (CH_2Cl_2)) after finishing each experiment. Potentials in the text are given with respect to the SCE.

The electrochemical instrumentation was a Princeton Applied Research Model 170 electrochemical system with an XY recorder. IR compensation was used throughout in CV experiments.

Preparation of [$Cp^*_2Fe_2S_4$]I_2. The brown solution of 600 mg (1.18 mmol) of I and 300 mg (1.18 mmol) of iodine in 75 mL of toluene was stirred for 60 min at room temperature. The resulting brown precipitate was filtered, washed with 10 mL each of toluene and ether, and vacuum dried to give IIb in 36% yield. By recrystallization from CH_2Cl_2 at −25 °C dark brown crystals of composition $Cp^*_2Fe_2S_4I_2\cdot 2CH_2Cl_2$ were obtained. ^1H NMR ($CDCl_3$): δ 1.62. Anal. Calcd for $C_{20}H_{30}Fe_2S_4I_2\cdot 2CH_2Cl_2$: C, 28.29; H, 3.67. Found: C, 28.36; H, 3.54; mol wt 934.06.

Preparation of [$Cp^*_2Fe_2S_4$][PF_6]$_2$. Method A. A 0.029-mL (0.56-mmol) sample of bromine was added to a solution of 285 mg (0.56 mmol) of I in 20 mL of toluene at room temperature. After the mixture was stirred for 2 h at room temperature, a bright brown precipitate was formed, which was filtered, washed with toluene and ether, and vacuum dried. The resulting powder (266 mg (0.4 mmol), mainly supposed to consist of [$Cp^*_2Fe_2S_4$]Br_2) was dissolved in 20 mL of H_2O, giving a green solution. After filtration, 129 mg (0.79 mmol) of NH_4PF_6 was added to this solution, resulting in a brown precipitate, which turned green after 2 h of stirring at room temperature. After filtration and washing with H_2O and ether, the product was vacuum dried to give IId in about 26% yield with respect to I.

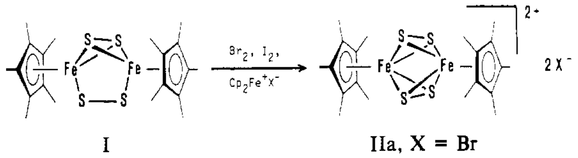
Method B. To a solution of 224 mg (0.44 mmol) of I in 20 mL of CH_2Cl_2 a solution of 290 mg (0.88 mmol) of [Cp_2Fe][PF_6] (Cp = η^5-C_5H_5) in 60 mL of CH_2Cl_2 was added. After the mixture was stirred for 30 min at room temperature, the solvent was evaporated. The resulting powder was twice extracted with 35 and 15 mL, respectively, of toluene to give a green-brown residue, which was washed with small amounts of CH_2Cl_2 to remove brown-green impurities. After the residue was dried under vacuum, a green powder was isolated containing IId in 61.5% yield. The filtrates of the extraction were concentrated. Chromatography on SiO_2 (column 10 × 3.5 cm) gave successively a yellow band containing Cp_2Fe (60%) and a brown band containing I (13.5%), both eluted with toluene. Complex IId was recrystallized from acetone/ether 10:1 (−25 °C) to give green compact needles.

IR (KBr): 1385 m, 1021 m (ν(CH)), 837 vs, 522 s (ν(PF)) cm^{-1}. ^1H NMR (acetone-d_6): δ 1.61. Anal. Calcd for $C_{20}H_{30}Fe_2S_4P_2F_{12}$: C, 30.02; H, 3.78; S, 16.02; P, 7.74. Found: C, 30.09; H, 3.80; S, 16.60; P, 8.01; mol wt 800.31. FD mass spectrum (CH_2Cl_2 solution): m/z 510, corresponding to $C_{20}H_{30}Fe_2S_4^{\cdot +}$.

Oxidation of I with $(C_5H_5)_2Fe^+BF_4^-$. [$Cp^*_2Fe_2S_4$][BF_4]$_2$ was prepared in the same manner as described above (method B) from 175 mg (0.34 mmol) of I. However, only 1 redox equiv of $Cp_2Fe^+BF_4^-$ was employed. The green crude product was recrystallized from CH_2Cl_2 to give 65 mg of [$Cp^*_2Fe_2S_4$][BF_4]$_2$ (56% yield based on redox equivalents consumed). ^1H NMR (acetone-d_6): δ 1.61. Anal. Calcd for $C_{20}H_{30}Fe_2S_4B_2F_8$: C, 35.12; H, 4.42. Found: C, 35.18; H, 4.44; mol wt 684.0.

Results

Syntheses. The reaction of $Cp^*_2Fe_2S_4$ (I) with Br_2 or I_2 leads to the formation of dark brown precipitates. These can unambiguously be identified as the dihalogen adducts of I only in the case of X = I$^-$ (eq 1) by means of analytical data. However, the hypothetical Br_2 adduct IIa, which is more soluble in polar solvents than IIb, can be transfered into the PF_6 salt IId, which now analyzes correctly. The transfer of IIa to IId by the addition of NH_4PF_6 occurs gradually and is accompanied by a color change from brown to green: an initially formed brown precipitate may be interpreted as consisting of the dication along with mixed Br$^-$ and PF_6^- anions.



(1)

I

IIa, X = Br
b, X = I
c, X = BF_4
d, X = PF_6

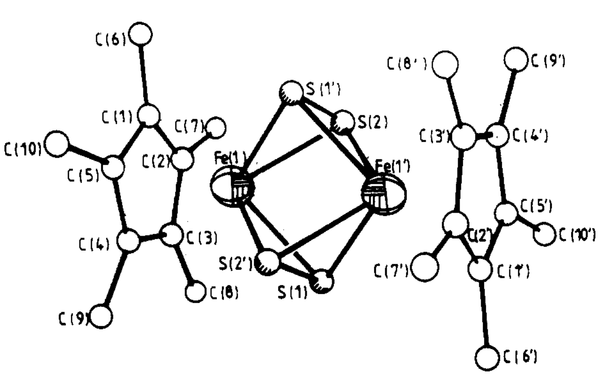


Figure 1. ORTEP drawing of the molecular structure of the dication of [$(C_5Me_5)_2Fe_2S_4$]$I_2\cdot 2CH_2Cl_2$ (IIb).

Table I. Atomic Coordinates for Complex IIb

	x/a	y/b	z/c
Fe1	0.5507 (1)	0.3968 (1)	0.4620 (1)
S1	0.6926 (3)	0.5163 (2)	0.5329 (1)
S2	0.4945 (3)	0.5602 (2)	0.4043 (1)
C1	0.505 (1)	0.2781 (7)	0.3739 (5)
C2	0.662 (1)	0.3200 (7)	0.3545 (5)
C3	0.757 (1)	0.3004 (7)	0.4189 (5)
C4	0.6588 (8)	0.2416 (5)	0.4803 (4)
C5	0.5029 (8)	0.2284 (5)	0.4532 (4)
C6	0.3732 (8)	0.2736 (6)	0.3215 (4)
C7	0.7189 (8)	0.3733 (6)	0.2726 (3)
C8	0.9311 (8)	0.3291 (6)	0.4170 (5)
C9	0.7132 (9)	0.1999 (6)	0.5578 (4)
C10	0.3671 (9)	0.1594 (6)	0.4944 (4)
C11	0.868 (1)	−0.0243 (7)	0.3110 (5)
I1	0.11236 (7)	0.15508 (4)	0.14545 (3)
Cl1	0.6680 (3)	0.0281 (2)	0.3140 (2)
Cl2	0.9571 (3)	0.0192 (2)	0.3960 (2)

Table II. Important Bond Distances (Å) and Angles (deg) for Complex IIb

Fe1–Fe1′	2.883 (3)	S1–S2′	2.014 (5)
Fe1–S1	2.278 (4)	S1′–S2	2.014 (5)
Fe1–S1′	2.282 (4)	S1···S2	2.894 (5)
Fe1–S2	2.275 (4)		
Fe1–S2′	2.272 (4)		
Fe1′–S1	2.282 (4)		
Fe1′–S2	2.272 (4)		
Fe1′–Fe1–S1	50.9 (1)	Fe1–S1–Fe1′	78.4 (1)
		Fe1′–S1–S2′	63.6 (1)
S1–Fe1–S2	78.9 (2)	Fe1–S2–Fe1′	78.1 (1)

The dicationic complex IIb can be reduced by equimolar amounts of Li_2S_2 or excess CH_3Li into neutral I in good yields. These reactions have been carried out in toluene/THF mixtures.

Spectroscopic Characterization. Only poor information can be drawn from IR and NMR spectra. Although S_2 ligands regardless of their coordination mode exhibit ν(S–S) frequencies in the 500-cm^{-1} region,[15] no ν(S–S) absorption can be detected for the dicationic species IIa–d (the corresponding ν(S–S) absorption of I appears at 520 cm^{-1} [7]). Only ν(CH) and ν(PF) frequencies are displayed in these cases. The ^1H NMR spectra indicate symmetrical structures for all compounds, with methyl resonances being not very susceptible to the charge change at the Fe_2S_4 core. A correct mass spectrum (field desorption technique) for the cationic part of the molecule, was only observed for the PF_6^- anion containing complex IId. In the other cases halogen-containing fragments have been observed, probably arising from chemical reactions on the emitter surface.

Molecular Structure of [$Cp^*_2Fe_2S_4$]I_2 (IIb). An X-ray diffraction analysis was carried out on a single crystal of IIb grown from CH_2Cl_2. An ORTEP drawing is shown in Figure 1; positional and important bond parameters are summarized in Tables I and

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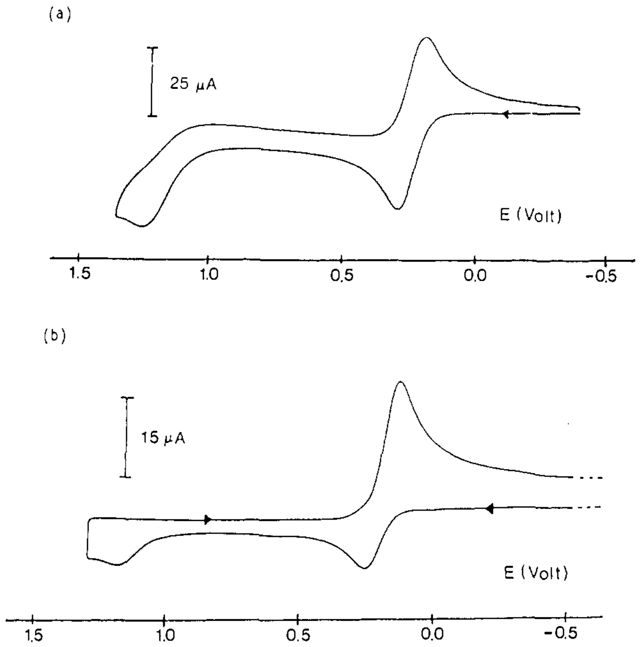


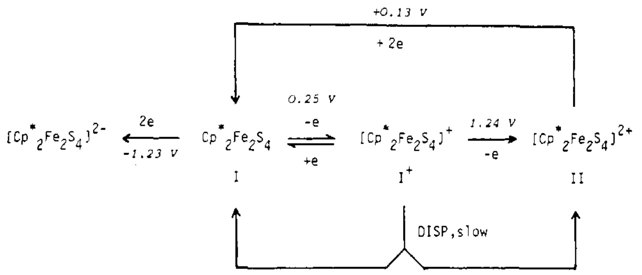
Figure 2. Cyclic voltammograms of 1×10^{-3} *m* solutions of $Cp^*_2Fe_2S_4$ (a) and $[Cp^*_2Fe_2S_4]^{2+}$ (b) in CH_2Cl_2 with $[(C_4H_9)_4N]PF_6$ (0.1 *m*) as supporting electrolyte (scan rate 0.1 V s^{-1}; potentials vs SCE). In trace b, the two-electron-reduction wave at −1.23 V is omitted.

II. The structure of IIb is characterized by a set of two parallel η^2-disulfur ligands, bridging the two Fe atoms, which are separated by 2.883 (3) Å from each other. The methyl groups of both Cp* rings are oriented in a staggered conformation as in the starting material I. Both anions were found not to be in a close contact to the sulfur ligands (the closest S–I distance is 3.479 (4) Å). The molecule is distinguished by an inversion center and contains two solvent molecules (CH_2Cl_2).

Thus, the main difference between the structures of I and IIb is the conversion of a η^1-S_2 bridge into a η^2-S_2 bridge accompanied by a remarkable shortening of the Fe–Fe distances on the order of 0.7 Å. These two alternative geometries have different electronic requirements. Due to qualitative MO considerations, I may formally be regarded as a Fe^{III} complex with the η^1-S_2 ligands as a four-electron donor.[16] A closed valence shell for each Fe atom can only be achieved by S to Fe p_π–d_π interactions. Oxidation of I may result at first in the removal of one electron from the Fe_2S_4 core, a step that may not significantly alter the geometry of the molecule.[17] The removal of a second electron apparently causes an electron deficiency, which can only be compensated by a 90° switch of the η^1-S_2 ligand into a η^2-S_2 ligand. The latter then provides four electrons with respect to each Fe atom on the basis of Fe^{IV}, thus giving rise to the formation of a closed shell without requiring any Fe–Fe bond. The observed distance of 2.883 (3) Å is not in contrast to this expectation because, usually, Fe–Fe bonds for bridged dimeric CpFe complexes do not exceed 2.54 Å.[18] Thus, the considerable shortening of the Fe–Fe distance when going from I to IIb may rather be a consequence of stereochemical constraints, caused by both η^2-S_2 bridges, than of electronic effects.

Electrochemistry and Related Studies. When I is reduced in a cyclic voltammetry experiment, a single irreversible reduction peak is found at −1.23 V (CH_2Cl_2/SCE). This observation may correspond to the already well-known cleavage of the η^2-S_2 ligand in $Fe_2(CO)_6S_2$ by strong reducing agents.[19] A more complex behavior, however, is found for the oxidation part. Thus, the cyclic voltammogram of I in CH_2Cl_2 (Figure 2a) shows a quasi-reversible one-electron oxidation at $E_{1/2}$ = +0.25 V and an irreversible one-electron oxidation at 1.24 V (vs saturated SCE), followed by further multielectron oxidation waves at more positive potentials not shown in the figure. On the contrary, the reduction of dication II (Figure 2b) is achieved in a single two-electron wave at E_{pc} = 0.13 V. The backward voltammetric scan of II is nearly identical with the foreward scan belonging to I. This invokes the existence of a monocation I^+ intermediate in the oxidation of I. The second oxidation peak in the voltammogram of I may be assigned to the oxidation of this monocation I^+ to II. If this is the case, however, the latter oxidation process must be accompanied by substantial decomposition since the backward peak at E_p = 0.2 V is not enhanced. Coulometric electrolysis of a solution of I at 0.6 V rapidly consumes 1 *F*/mol, but a small current continues to flow at this potential. A cyclic voltammogram at this stage looks as if it were composed of a CV of I and a CV of II. When the solution is further oxidized at the foot of the second wave, the green solution of II is obtained, which has a voltammogram identical with that in Figure 2b. Finally, complex I can be regenerated by coulometrical two-electron reduction. All attempts to isolate the proposed monocation I^+ by controlled-potential electrolysis of I failed, the only isolable cationic compound being II. It thus appeared that there was a disproportionation pathway for the generation of I and II from I^+, which is not seen on the time scale of cyclic voltammetry. The overall scheme for the electrochemistry of I in CH_2Cl_2 is summarized in Scheme I. This view was further confirmed by the chemical oxidation of I with $Cp_2Fe^+BF_4^-$ in dichloromethane: only $[Cp^*_2Fe_2S_4][BF_4]_2$ (IIc) was formed together with ferrocene and unreacted or newly formed I.

Scheme I



The electrochemical oxidation, in acetonitrile, of the complex $Cp_2Fe_2(SEt)_2(S)_2$, which is isoelectronic with and structurally closely related to I, was reported to cause the complex to lose the disulfur ligand and to form a diacetonitrile complex.[8] We have therefore also investigated the electrochemistry of I and II in this nucleophilic solvent. The overall electrochemistry with I and II being the stable oxidation states is completely retained as proved by controlled-potential coulometry, which means that there is no acetonitrile incorporation accompanying the oxidation of I. However, the voltammograms in Figure 3 show interesting differences compared to those in dichloromethane solvent concerning the intermediate processes. Now, the oxidation of I is no longer a pure quasi-Nernstian process, but the backward peak splits into two waves at E_p = 0.17 and 0.07 V. These two waves merge into one broad wave at slower sweep rates. Furthermore, the second oxidation peak is now at +0.67 V, almost 600 mV more negative than in dichloromethane. This behavior also emerges when acetonitrile is gradually added to a dichloromethane solution of I. In particular, the peak at 0.67 V is growing at the expense of the +1.24 V peak of Figure 2. Again, the reduction of II occurs at E_{pc} = 0.07 V in a single two-electron wave with an identical backward trace as shown in the forward scan of I.

We suggest that the nucleophilic solvent acetonitrile assists in the oxidation of I^+ and in the process of reorientation of the disulfur ligand. Thus, the oxidation potential of I^+ may be facilitated by the formation of an intermediate acetonitrile complex $I^{+\prime}$. This would explain the dramatic lowering of the oxidation potential and also the acceleration of the disproportionation pathway of I^+ such that the resulting peak becomes detracted in the cyclic voltammogram. Thus, according to Scheme II, the

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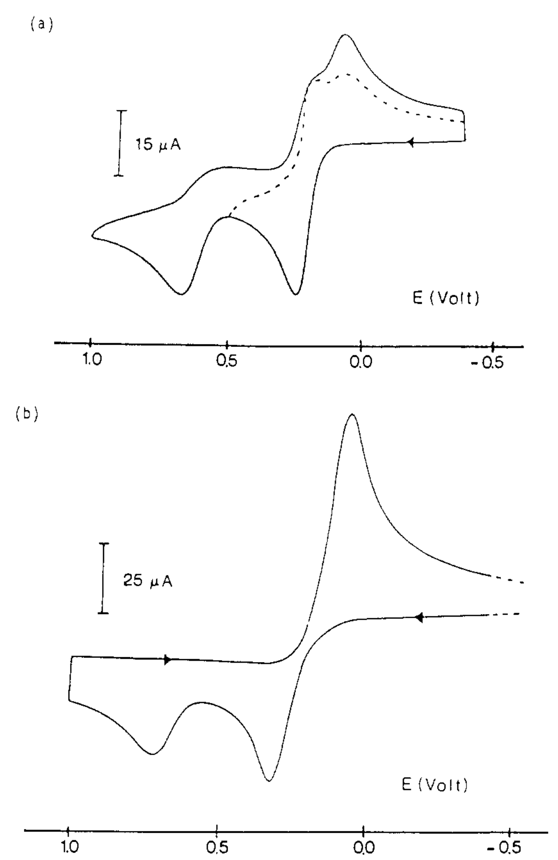
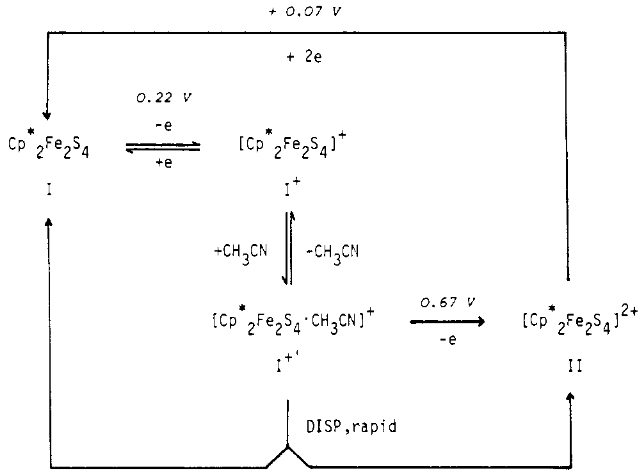


Figure 3. Cyclic voltammograms of 1×10^{-3} *m* solutions of $Cp^*_2Fe_2S_4$ (a) and $[Cp^*_2Fe_2S_4]^{2+}$ (b) in CH_3CN with $[(C_4H_9)_4N]PF_6$ (0.1 *m*) as supporting electrolyte (scan rate 0.2 V s^{-1}; potentials vs SCE).

Scheme II

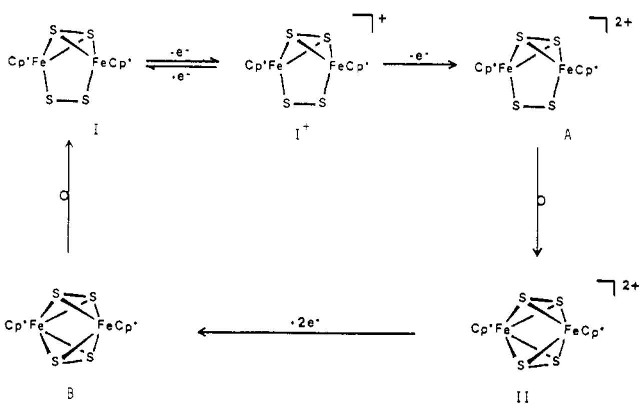


second reduction peak at $E_p = 0.07$ is due to II formed by the disproportionation route, and the magnitude of this peak is enhanced when the second oxidation peak of I is included in the scan and II is directly produced by electrochemical oxidation of $I^{+\prime}$. A similar redox behavior of I was found in dichloromethane when an equimolar amount of the nucleophilic $NBu_4^+I^-$ was added.

Discussion

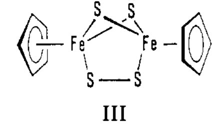
The dicationic complex $Cp^*_2Fe_2S_4^{2+}$ (II) was produced from neutral $Cp^*_2Fe_2S_4$ (I) by chemical and electrochemical methods. It can also be reduced in a similar way to neutral I. These reactions involve a reversible η^1-$S_2 \rightleftarrows \eta^2$-$S_2$ rearrangement, which resembles to some extent the already well-investigated acetylene rotation in parallel- and perpendicular-bridged C_2H_2-complexes.[20] Hitherto known examples of S_2 conversions have either been induced by a change in the coordination sphere of the metal centers or the sulfur ligands in $Cp_2V_2(\eta^1\text{-}S_2)(S)_2$.[2,21] The driving force in these reactions obviously was the compensation of the strong electron deficiency at the V centers. On the basis of our results we assume electron-transfer processes to be the key steps in the system I/II. On the time scale of cyclic voltammetry the monocation I^+ is a stable species as shown by the reversible wave, but it disproportionates to give I and IId in a slower electron-transfer reaction. Thus, although the direct oxidation of I^+ at the electrode requires rather positive potentials (+1.25 V in CH_2Cl_2 or +0.67 V in CH_3CN), for quantitative bulk oxidation of I to IIc,d an oxidizing agent with a redox potential just sufficient to create the monocation will do.

Scheme III



Electron-transfer processes may also induce the rearrangement of one of the S_2 bridges observed in the conversion of I to II. The fast reversible one-electron oxidation of I indicates that the ligand reorientation does not yet occur in this step. Further oxidation, however, leads to an obviously unfavorable electron configuration of each Fe atom as represented in formula A (Scheme III), which is expressed by the very positive irreversible oxidation step observed in the CV experiment. A cannot be detected on the time scale of cyclic voltammetry, but its rearrangement product IId, which now possesses 18-electron configurations for both Fe centers, can be. For the reduction of II an immediate two-electron process is evident, which would lead to unfavorable 19-electron Fe configurations (formula B, Scheme III). The final rearrangement leads back to I in which the electrondeficiency is balanced by d_π–p_π Fe–S interactions.[22] The way in which this reaction pathway is assisted by nucleophiles is, however, not yet well understood.

In conclusion this work demonstrates that electron-transfer processes give rise to the unprecedented reversible η^1-$S_2 \rightleftharpoons \eta^2$-$S_2$ rearrangement. It is also evident that the redox chemistry of the Fe_2S_4 core sensitively depends on slight modifications of the ligand sphere when I is compared to the already carefully investigated $Cp_2Fe_2(SEt)_2(S_2)$ (III).[16] Thus, the presence of the permethylated cyclopentadienyl ring with its enhanced donating activity and the presence of a η^2-S_2 ligand instead of two SR bridges may stabilize the other S_2 ligand in a way that elimination is no longer possible even under strong oxidation conditions.



III

Registry No. I, 99248-81-4; IIa, 114299-79-5; IIb, 114299-78-4; IIc, 114299-82-0; IId, 114299-81-9.

Supplementary Material Available: A table of hydrogen coordinates and thermal parameters (Table SI) (3 pages); a table of calculated and observed structure factors (Table SII) (10 pages). Ordering information is given on any current masthead page.

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(20) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

(21) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 7800.

(22) Here, the S_2^{2-} ligands are regarded as four- and eight-electron donors, respectively.