

# New $\pi$ -Extended 1,1'-Disubstituted Ferrocenes with Thioate and Dithioate End Groups

Sinem-Fatma Schmiel<sup>[a]</sup> and Holger Butenschön<sup>\*[a]</sup>

*Dedicated to the Memory of Professor Dr. Klaus Banert*

Extended  $\pi$  systems based on 1,1'-aryl or (2-arylethynyl) disubstitution at ferrocene with thioate or dithioate end groups are reported. In the context of molecular electronics, such end groups are possible alternative end groups for the attachment of molecular wires at gold surfaces. The respective thioates were successfully prepared in high yields via the respective carboxylic acid derivatives. Subsequent treatment with Lawesson's reagent led to the respective dithioates. However, this

did not work in the presence of triple bonds, in these cases, product mixtures were formed. On the basis of literature evidence with Woollin's reagent, the selenium analog of Lawesson's reagent, one product was tentatively characterized as a double cyclization product of two triple bonds and two molecules of Lawesson's reagent. Preliminary experiments towards the formation of gold complexes by reaction with a Johnphos gold(I) salt are included.

## Introduction

Expanded  $\pi$  systems deserve interest in the context of aromaticity, photophysical properties, molecular electronics, electronic organic materials such as conducting polymers, organic magnetic materials or nonlinear optics, and a number of other fields.<sup>[1–3]</sup> Although spherical structures such as curved or twisted polycyclic aromatic hydrocarbons and also fullerenes are actively being investigated,<sup>[4–8]</sup> most of the extended  $\pi$  systems consist of six-membered rings and are more or less planar. Ferrocene is a three-dimensional electron-rich organometallic aromatic compound, which was discovered almost 70 years ago.<sup>[9,10]</sup> The chemistry of ferrocene has been the subject of continuing research under various aspects,<sup>[11–18]</sup> such as stereoselective catalysis,<sup>[19–24]</sup> redox chemistry,<sup>[25]</sup> C–H activation,<sup>[26–29]</sup> materials chemistry,<sup>[30–39]</sup> bioorganic and medicinal chemistry.<sup>[30,40–49]</sup> The facile rotation of the cyclopentadienyl ligands renders ferrocene moieties in many derivatives conformationally flexible.<sup>[50]</sup>

In the context of molecular electronics<sup>[51,52]</sup> oligophenyleneethynylenes (OPEs) such as **1** (Scheme 1) and related molecular wires<sup>[53,54]</sup> have been constructed and applied, for example, in mechanically controllable break junction (MCBJ) measurements.<sup>[55–58]</sup> OPEs are rather rigid linear molecules with a fixed length. In addition, they are more or less flat thus

possibly undergoing intermolecular  $\pi$ - $\pi$  interaction.<sup>[3,59–61]</sup> Replacement of some, not all, of the phenylene moieties by 1,1'-ferrocenylidene building blocks would render the molecular wires three-dimensional and thus less prone for  $\pi$ , $\pi$  stacking. Limited conformational flexibility would allow for an adjustment of the length of a wire to an electrode distance, comparable to hinges in a folding rule.<sup>[62]</sup> In addition, ferrocene units are redox-active thereby facilitating the transport of electrons.<sup>[63]</sup> Based on this idea we have earlier prepared a number of alkynylferrocenes containing one or more ferrocene moieties, for example, compounds **2** and **3** (Scheme 1).<sup>[62,64–69]</sup>

Molecular wires such as OPEs usually bear end groups with functionalities allowing for an attachment at an electrode material, often gold. In particular, sulfur-containing end groups such as thioacetyl groups as in **1** or **2** are well established, they are converted into thiol groups on a gold surface allowing for charge transport.<sup>[55,70,71]</sup> We prepared some alkynylferrocenes bearing thioacetyl groups,<sup>[64]</sup> but found out that these are rather sensitive and often did not stand necessary reaction or purification conditions. Based on a paper by Mayor et al.<sup>[72]</sup> describing the bromine catalyzed transformation of *tert*-butylsulfanyl groups into thioacetyl units we synthesized some ferrocene-based molecular wires with *tert*-butylsulfanyl end groups such as the photochemically switchable **3** (Scheme 1).<sup>[62,67,69]</sup> These are stable compounds, however, it was not possible to convert them to the respective thioacetyl derivatives due to dominating redox reactions between the ferrocene units and the bromine catalyst.

Next, we focused on dithioate end groups. This was stimulated by the results of Borguet et al.,<sup>[73,74]</sup> who investigated porphyrin-based molecular wires with either two thiol or two dithioate end groups and reported an improved junction to a gold surface and an up to ten-fold enhancement of the charge transport as compared to thiol end groups with the hapticity of the dithioate coordination being critical: Three distinct conductance values were obtained standing for bidentate/bidentate, bidentate/monodentate and monodentate/monodentate

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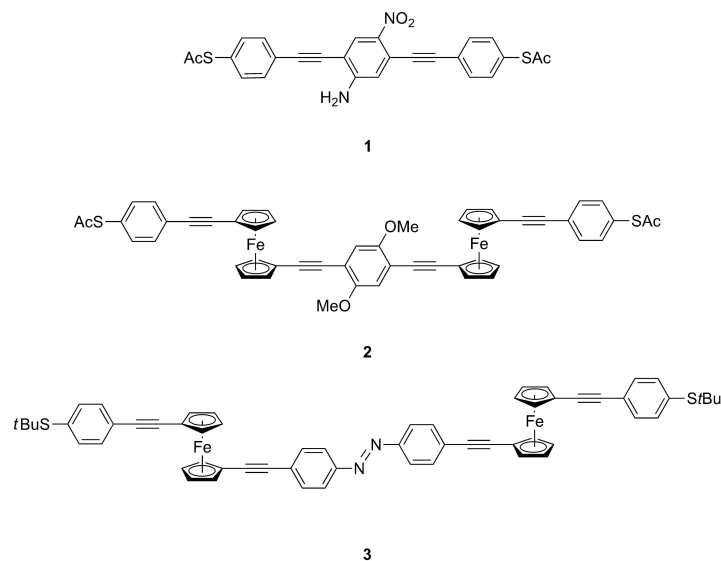
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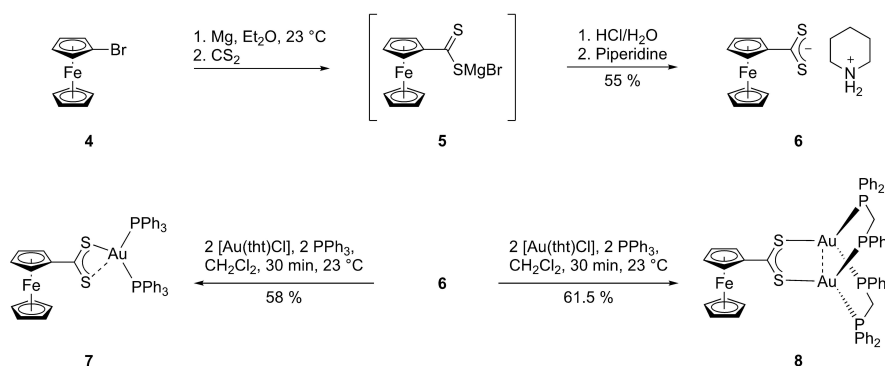
Supporting information for this article is available on the WWW under <https://doi.org/10.1002/ejoc.202100335>



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Scheme 1. Examples of an OPE (1) and ferrocene based OPEs (2, 3).



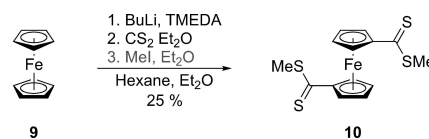
Scheme 2. Synthesis of ferrocenyldithioate gold complexes **7** and **8** according to Roesky et al.<sup>[75]</sup>

coordination at the two gold electrodes with the first combination giving the best results. An important paper in this context was published by Roesky et al. in 2014, who reported ferrocenyldithioates coordinated at gold. Complexes **7** and **8** were obtained by treatment of bromoferrocene (**4**) with magnesium followed by quench with carbon disulfide. Subsequent treatment with hydrochloric acid followed by piperidine gave piperidinium dithioate **6** in 55% yield. The anion of **6** was coordinated at gold by reaction with chloro (tetrahydrothiophene)gold(I) in the presence of either triphenylphosphane or bis(diphenylphosphino)methane giving complexes **7** and **8** in 58% and 61.5% yield, respectively (Scheme 2).<sup>[75]</sup>

While the ferrocenyldithioate ligand is known, this is not the case for ferrocene-1,1'-bis(dithioates) nor for ferrocene-based molecular wires with dithioate end groups. Therefore we investigated ferrocene-based molecular wires with two dithioate end groups.

## Results and Discussion

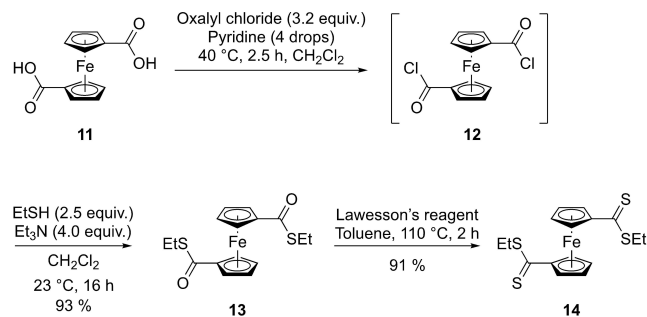
In a first attempt, we followed the route devised by Roesky et al.<sup>[75]</sup> and treated 1,1'-dibromoferrocene with magnesium followed by carbon disulfide, hydrochloric acid, and piperidine in order to obtain the 1,1'-disubstituted analog of **6**. However, we could not isolate any defined product. Therefore, we resorted to a 1,1'-dilithiation of ferrocene (**9**) followed by addition of carbon disulfide and quench with iodomethane. This procedure afforded dimethyl ferrocene-1,1'-bis(carbodithioate) (**10**) in 25% yield as the first derivative of ferrocene-1,1'-bis(carbodithioic acid) (Scheme 3). **10** was charac-



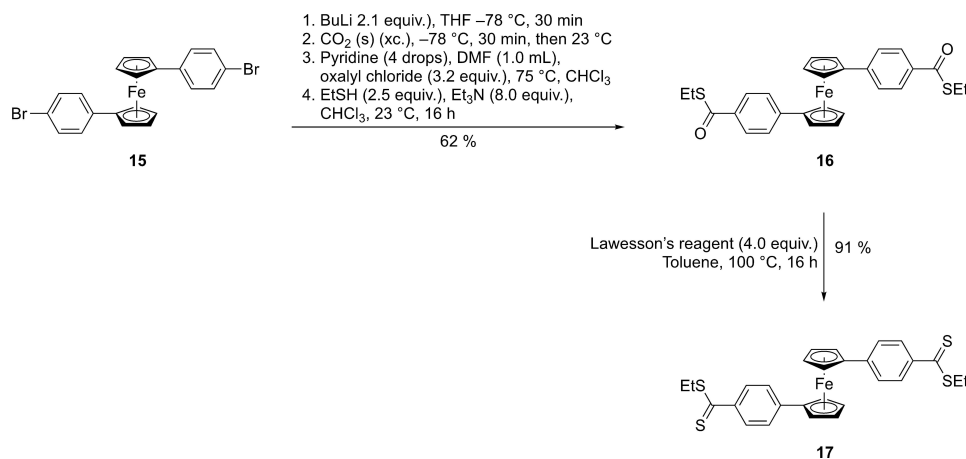
Scheme 3. Synthesis of dimethyl ferrocene-1,1'-bis(carbodithioate) (**10**).

terized spectroscopically with a  $^{13}\text{C}$  NMR resonance of the thiocarbonyl carbon atoms at  $\delta = 225.3$  ppm.

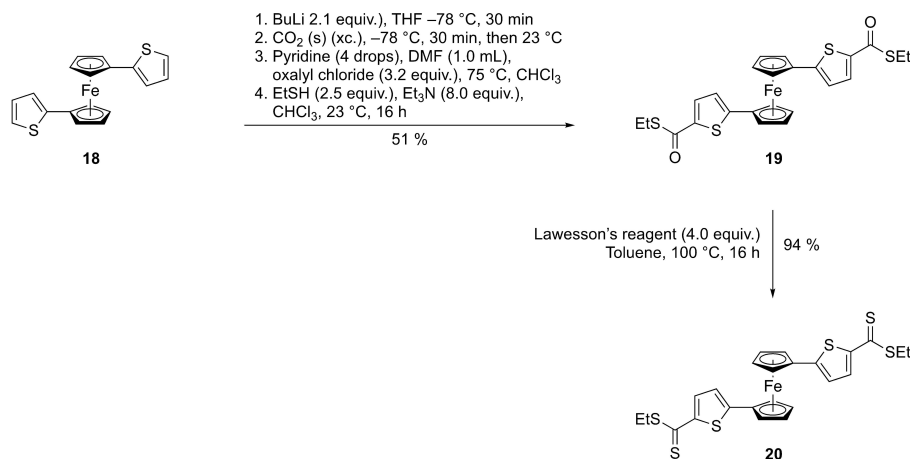
In an alternative approach, the closely related diethyl diester **14** was obtained by treatment of ferrocene-1,1'-bis(carboxylic acid)<sup>[76]</sup> (**11**) with oxalyl chloride affording acyl chloride **12**, which was not isolated but treated with ethanethiol giving thioester **13** in 93% yield. Subsequent reaction with Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-



Scheme 4. Synthesis of diethyl ferrocene-1,1'-bis(carbodithioate) (**14**).



Scheme 5. Synthesis of diethyl ferrocene-1,1'-bis(phenyl-4-carbodithioate) (**17**).



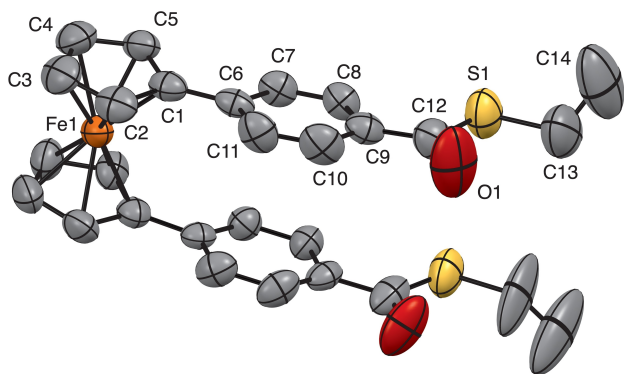
Scheme 6. Synthesis of diethyl ferrocene-1,1'-bis(2-thienyl-4-carbodithioate) (**20**).

2,4-dithione)<sup>[77]</sup> gave diethyl bis(dithioate) **14** in 91% yield (Scheme 4).

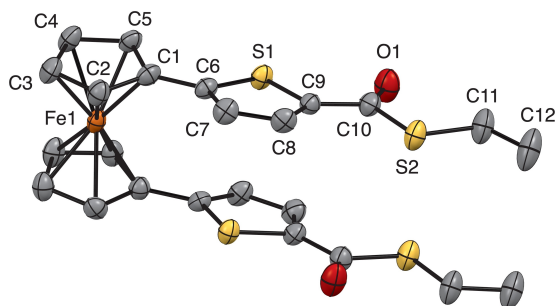
In a similar way, the more extended  $\pi$  system **17** was prepared by treatment of 1,1'-di(4-bromophenyl)ferrocene<sup>[65]</sup> (**15**) with butyllithium at low temperature followed by solid  $\text{CO}_2$ . Without isolation of the dilithium dicarboxylate formed the mixture was treated with oxalyl chloride in the presence of a small amount of pyridine and DMF affording the diacid dichloride, which was also not isolated. The addition of ethanethiol and triethylamine gave thioester **16** in 62% yield. Following treatment of **16** with Lawesson's reagent afforded diethyl bis(dithioate) **17** in 91% yield (Scheme 5).

In addition to **17**, the thiophene-based analog **20** was prepared via **19** using a similar protocol starting from 1,1'-di(2-thienyl)ferrocene<sup>[78]</sup> (**18**) (Scheme 6). Compounds **19** and **20** deserve interest, because the thiophene building blocks may act as additional ligating moieties.

Crystallization from dichloromethane (1 mL) covered by a layer of hexane (5 mL) afforded crystals suitable for crystal structure analyses of thioates **16** and **19** (Figure 1 and Figure 2).



**Figure 1.** Structure of **16** in the crystal.<sup>[79]</sup> H atoms are omitted for clarity. Ellipsoids at 50% probability level. Selected bond lengths [pm], bond angles [°] and torsional angles [°]: Fe1–C1 206.9(4), Fe1–C2 203.5(3), Fe1–C3 204.4(4), Fe1–C4 204.4(4), Fe1–C5 204.6(5), C1–C2 142.1(5), C2–C3 140.8(5), C3–C4 139.9(7), C4–C5 140.2(6), C1–C6 146.2(5); C9–C12–O1 122.0(4), C9–C12–S1 116.5(3), C12–S1–C13 104.3(3); C2–C1–C6–C11 11.0(5), C8–C9–C12–S1 –1.5(5), C10–C9–C12–O1 –0.7(6).



**Figure 2.** Structure of **19** in the crystal.<sup>[79]</sup> H atoms are omitted for clarity. Ellipsoids at 50% probability level. Selected bond lengths [pm], bond angles [°] and torsional angles [°]: Fe1–C1 207.5(4), Fe1–C2 206.3(5), Fe1–C3 204.1(5), Fe1–C4 204.1(4), Fe1–C5 204.9(4), C1–C6 145.4(7), C6–C7 138.0(7), C7–C8 139.4(7), C8–C9 136.8(9), C6–S1 171.3(5), C9–S1 171.7(5); C9–C10–O1 122.5(5), C9–C10–S2 114.6(4), C10–S2–C11 99.8(3); C2–C1–C6–C7 –13.8(8), C5–C1–C6–S2 –13.9(8), C8–C9–C10–S2 4.3(7), S1–C9–C10–O1 3.5(7).

Compound **16** adopts an eclipsed conformation with the aryl substituents next to one another. The conformation shows an approximate plane of symmetry through the iron atom and between the aryl groups, which have a centroid distance of 354.3 pm from one another. The cyclopentadienyl ligands show a centroid distance of 331.0 pm. The aryl substituents deviate from coplanarity with the cyclopentadienyl ligands by 11.0°. The distance Fe1–C1 is a little bit longer than most of those between the iron atom and the other cyclopentadienyl carbon atoms; this is presumably due to a steric repulsion of the substituents and is continued by a growing distance between the respective phenyl rings and between the attached thioate groups.

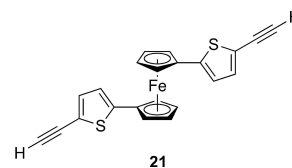
The structure of **19** resembles that of **16** in its eclipsed conformation with the thienyl substituents next to one another. However, the geometry is better described by an approximate twofold axis of rotation through the iron atom with the thienyl sulfur atoms and as well as the carbonyl oxygen atoms being transposed into one another, respectively. While the cyclo-

pentadienyl ligands show an average distance of 332.0 pm from one another, the centroid distance between the thienyl groups is 378.3 pm, which is closer than the centroid distance of the aryl substituents in **16**. Presumably, the thienyl rings exert a dipole moment placing the sulfur atoms away from one another thus resulting in some attractive interaction between these rings. The thienyl groups deviate from coplanarity with the cyclopentadienyl ligands by about 13°; the thioate groups are almost coplanar with the thienyl rings. The structure of **19** resembles that determined for the 1,1'-dithienylferrocene derivative **21** (Scheme 7).<sup>[65]</sup>

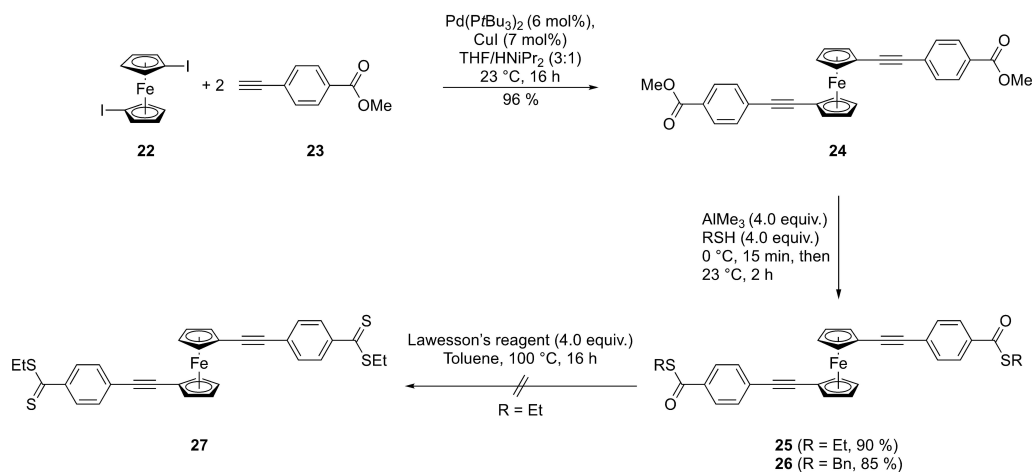
In order to obtain a more extended  $\pi$  system and in complementation of our earlier investigations<sup>[62,64,67–69,80]</sup> we envisaged a system with additional triple bonds between the ferrocene and the arene or thiophene moieties in **17** or **20**. To achieve this, 1,1'-diiodoferrocene<sup>[81,82]</sup> (**22**) was subjected to a Sonogashira coupling according to Long et al.<sup>[83]</sup> with methyl 4-ethynylbenzoate (**23**), which had been prepared according to Willis et al.<sup>[84]</sup> in an improved yield of 98%. The methyl ester **24** was obtained in 96% yield with no mono-substitution product observed. Ethyl and benzyl di(thioates) **25** and **26** were obtained from **24** in 90% and 85% yield, respectively, by treatment with trimethylaluminum and the respective thiol following a procedure by Wojtasek et al.<sup>[85]</sup> When **25** was treated with Lawesson's reagent in order to obtain the respective bis(dithioate) **27**, no defined product was obtained. Instead, a complex mixture of at least six compounds was obtained. A mass spectrum of the crude product mixture showed an increase in molecular weight to  $m/z=1146.0$  indicating some addition of Lawesson's reagent to the starting material (Scheme 8). The use of phosphorus(V) sulfide gave no reaction.

In an attempt to prepare the respective thiophene-derived compounds 1,1'-diiodoferrocene (**22**) was treated with 2-ethynylthiophene (**28**) in a Sonogashira coupling affording 1,1'-di(2-thienylethynyl)ferrocene (**29**) in 91% yield. The protocol used in the synthesis of **19** from **18** was applied here, giving di(thioate) **30** in 43% yield without isolation of the intermediates. However, subsequent treatment of **30** with Lawesson's reagent met with failure resulting in a complex mixture of ca. five compounds with consumption of **30** (Scheme 9). As before use of phosphorus(V) sulfide gave no reaction.

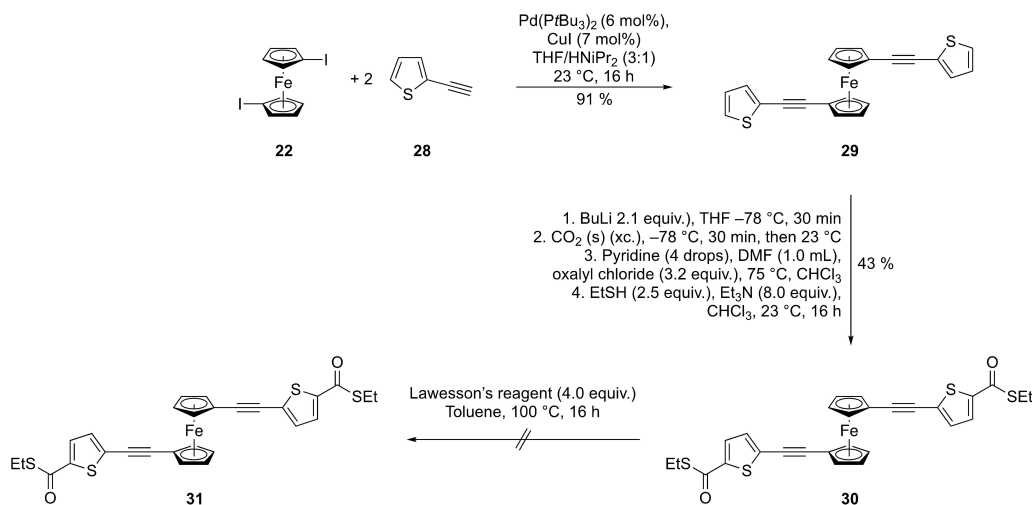
Based on mass spectra, <sup>1</sup>H, and <sup>13</sup>C NMR spectra one of the products formed was tentatively characterized as **32** or **33**, the symmetrical substitution pattern being in accord with the symmetry reflected by the <sup>1</sup>H and <sup>13</sup>C NMR spectra (Scheme 10). Chemical shifts, couplings, and integrations are in accord with **32** or **33**, with **33** being more likely for steric reasons. However,



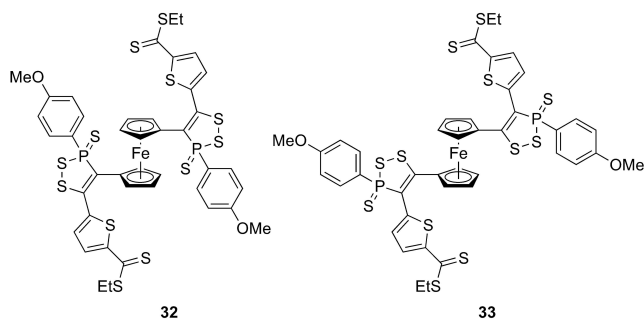
**Scheme 7.** 1,1'-Dithienylferrocene derivative **21**.



Scheme 8. Attempted synthesis of 27.



Scheme 9. Attempted synthesis of 31.



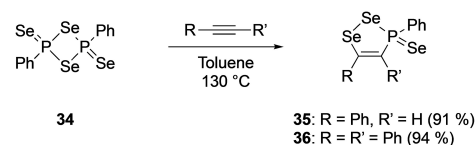
Scheme 10. Tentative constitutions of the reaction product of 30 and Lawesson's reagent.

no crystals suitable for a structure analysis could be obtained, so that a final assignment cannot yet be made.

Reactions of alkynes with Lawesson's reagent giving heterocyclic products have so far not been reported. However, a related reaction of a selenium analog (Woollins' reagent, 35)

with phenyl or diphenylethyne gave rise to a similar reactivity affording 36 and 37 in 91% and 94% yield, respectively (Scheme 11).<sup>[86]</sup> Obviously, alkynylferrocenes based thioates do not react with Lawesson's reagent with the formation of dithioates but undergo more complicated reactions with the triple bonds.

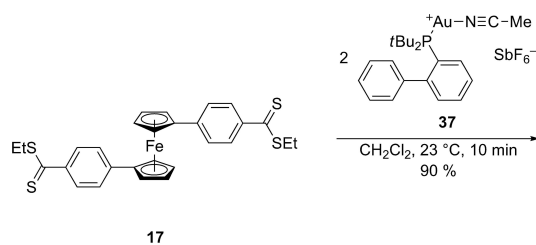
First experiments directed to a coordination of bis(dithioates) 17 and 20 at gold were undertaken with gold sources such as (dimethylsulfide)gold chloride giving products readily decomposing to the starting material. However, treat-



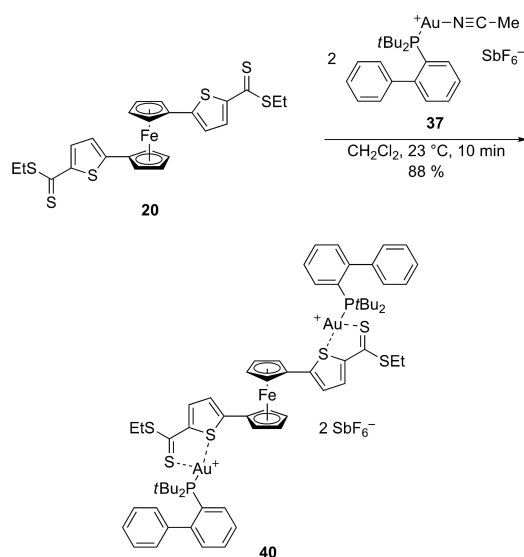
Scheme 11. Reaction of Woollins' reagent (34) with alkynes.<sup>[86]</sup>

ment of **17** and **20** in dichloromethane with the commercially available (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphane]gold (I) hexafluoroantimonate(V) [JohnPhosAu(MeCN)SbF<sub>6</sub>, **37**]<sup>[87]</sup> as the gold source resulted in color changes from red to green and from deep red to turquoise, respectively. The products were isolated as solids in high yields, no crystals suitable for crystal structure analyses were obtained. As mass spectrometric analyses showed the respective ligand signals only, the characterization relies on the NMR spectra obtained. In both cases, signal shifts and signal integration as well as the number of signals indicate a twofold coordination in accord with constitutions **39** and **40**, respectively (Scheme 12 and Scheme 13).

As an example, the spectra of **40** will be discussed here: The <sup>1</sup>H NMR spectra of **20** (red) and of **40** (blue) are compared in Figure 3. The signals of complex **40** show a coordination shift to lower field by  $\Delta\delta = 0.2\text{--}0.4$  ppm. In addition, signals of **40** in the aromatic region and intense doublets at  $\delta = 1.38$  ppm are



Scheme 12. Synthesis of gold complex **39**.



Scheme 13. Synthesis of gold complex **40**.

assigned to the JohnPhos ligand at gold. Figure 4 shows the comparison of the respective <sup>13</sup>C NMR spectra, which also show coordination shifts, particularly for those carbon atoms close to the coordinated sulfur atoms. Their respective coordination shifts for **40** are listed in Table 1. In analogy, the respective <sup>13</sup>C NMR data for **17** and **39** are given in Table 2.

Redox properties of some of the compounds prepared were investigated by cyclic voltammetry. As representative examples, the cyclic voltammograms of the related compounds **16**, **17**, and **39** are shown in Figure 5, Figure 6, and Figure 7. In addition, the numerical data of these compounds as well as those of the corresponding thiophene-based compounds **19**, **20**, and **40** are given in Table 3.

All of the voltammograms show reversible redox processes at half-wave potentials >0.1 V, which are assigned to the ferrocene moieties, and which indicate some electron withdrawal from the ferrocene moieties by the phenyl substituents bearing thioester or dithioester groups in the *para* positions. The data for **39** as well as for **40** are higher than those of **18** and **20** by 0.0686 V and by 0.1786 V, respectively, indicating an increased electron withdrawal due to the coordination at gold. The larger difference in the case of **40** may be attributed to the different modes of coordination as compared to **39**.

Table 1. <sup>13</sup>C NMR (400.1 MHz, CDCl<sub>3</sub>) chemical shifts  $\delta$  and coordination shifts  $\Delta\delta$  of selected carbon atoms in **20** and **40** in ppm; Cp=cyclopentadienyl.

Carbon atom	$\delta$ ( <b>20</b> ) [ppm]	$\delta$ ( <b>40</b> ) [ppm]	$\Delta\delta$ [ppm]
C=S	211.6	210.5	1.1
CH <sub>3</sub> -CH <sub>2</sub> -S	30.4	33.6	3.2
Cp-C-S	152.1	159.3	7.2
S=C-C-S	148.7	143.5	-5.2

Table 2. <sup>13</sup>C NMR (400.1 MHz, CDCl<sub>3</sub>) chemical shifts  $\delta$  and coordination shifts  $\Delta\delta$  of selected carbon atoms in **17** and **39** in ppm; Cp=cyclopentadienyl.

Carbon atom	$\delta$ ( <b>17</b> ) [ppm]	$\delta$ ( <b>39</b> ) [ppm]	$\Delta\delta$ [ppm]
C=S	226.9	235.8	8.8
CH <sub>3</sub> -CH <sub>2</sub> -S	31.4	35.2	3.8
S=C-C	142.8	128.2	-14.6

Table 3. Cyclic voltammetry data of selected compounds.  $E_{pc}$ =cathodic peak potential;  $E_{pa}$ =anodic peak potential;  $\Delta E = E_{pc} - E_{pa}$ ; half wave potential  $E_{1/2} = (E_{pc} + E_{pa})/2$ ; scan rate  $\nu = 100$  mV/s; c(TBAP)=0.1 mol/L in dichloromethane (TBAP=tetrabutylammonium phosphate), c(compound) = 0.005 mmol/L;  $T = 296$  K; potentials vs. FcH/FcH<sup>+</sup>.

Compound	$E_{pc}$ [V]	$E_{pa}$ [V]	$\Delta E$ [V]	$E_{1/2}$ [V]
<b>17</b>	0.2012	0.0629	0.1383	0.1320
<b>18</b>	0.1748	0.0328	0.1420	0.1038
<b>38</b>	0.2371	0.1077	0.1294	0.1724
<b>19</b>	0.2616	0.1196	0.1420	0.1906
<b>20</b>	0.2702	0.1107	0.1595	0.1905
<b>40</b>	0.4325	0.3058	0.1267	0.3691

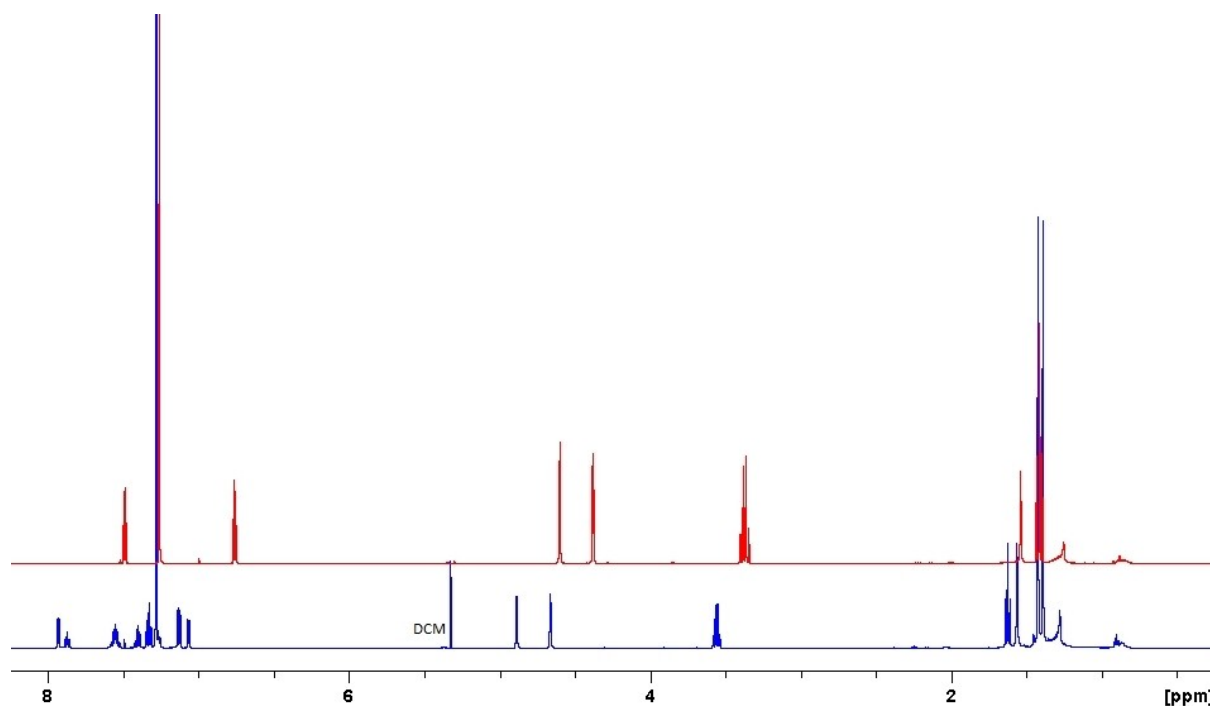


Figure 3. Comparison of the  $^1\text{H}$  NMR spectra (400.1 MHz,  $\text{CDCl}_3$ ) of **20** (red) and **39** (blue); DCM = dichloromethane.

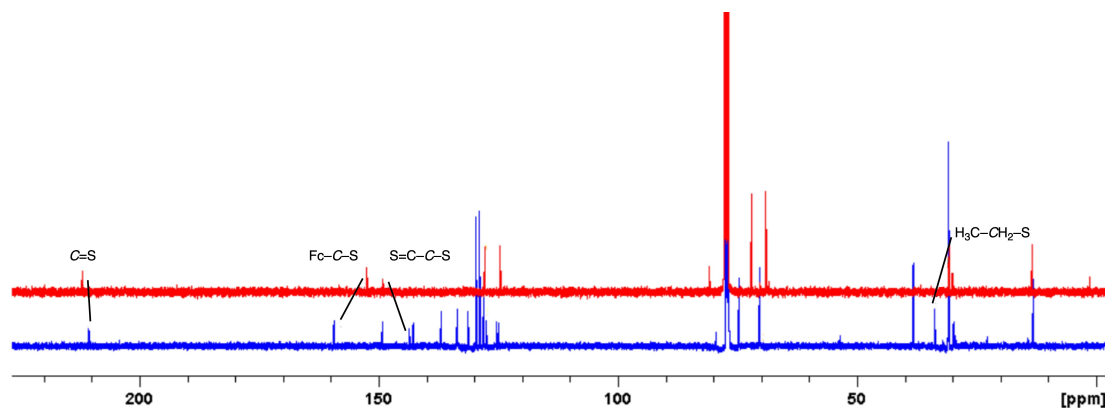


Figure 4. Comparison of the  $^{13}\text{C}$  NMR spectra (100.6 MHz,  $\text{CDCl}_3$ ) of **20** (red) and **40** (blue) with selected signal shifts.

## Conclusion

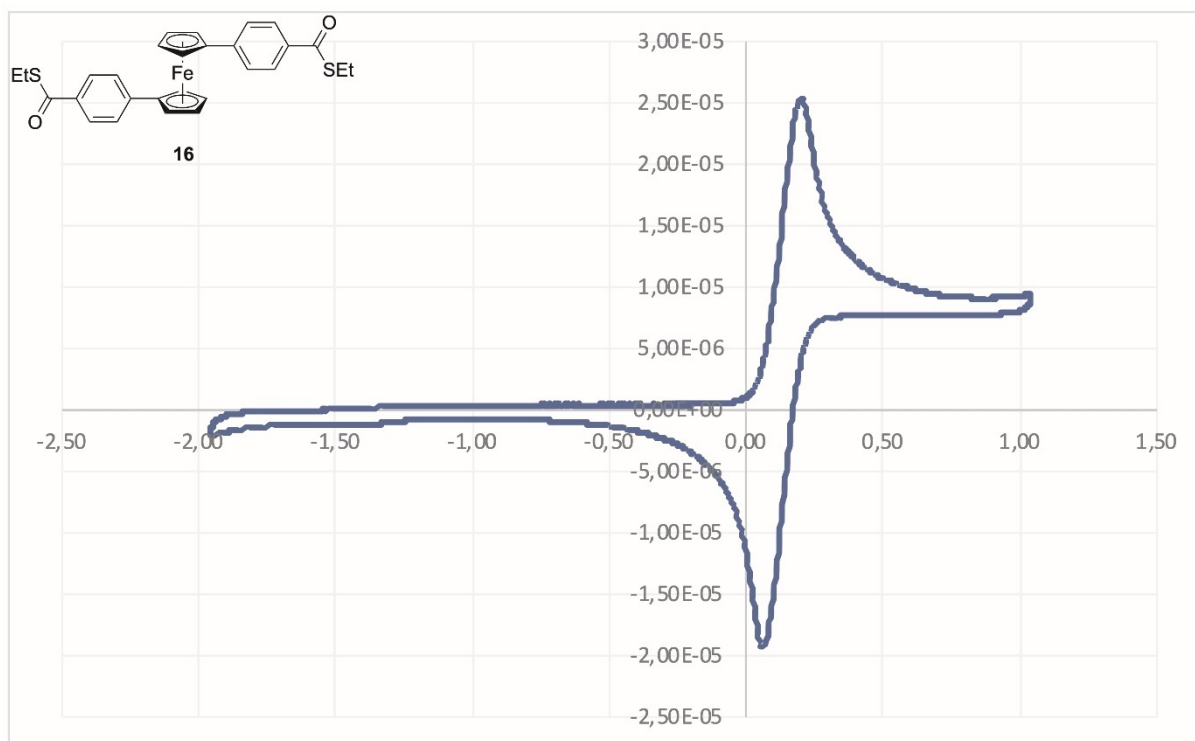
In conclusion, we have prepared some new ferrocene-based extended  $\pi$  systems with thioate or dithioate end groups attached at either one of the cyclopentadienyl ligands. While a first representative was prepared in moderate yield by a 1,1'-dilithiation of ferrocene followed by treatment with carbon disulfide, higher yields were achieved by routes via the carboxylic acid derivatives leading to thioates. Treatment with Lawesson's reagent gave the respective dithioates. Remarkably, this last step met with failure for thioates containing triple bonds. Product mixtures were obtained in these cases, one compound being tentatively identified as the product of a double cyclization between Lawesson's reagent and the triple

bonds. A similar product had earlier been obtained from a reaction of alkynes with the selenium analog, Woollin's reagent.<sup>[86]</sup> Preliminary experiments directed towards the formation of gold complexes indicate that these form upon treatment of two thioates with a Johnphos gold(I) salt.

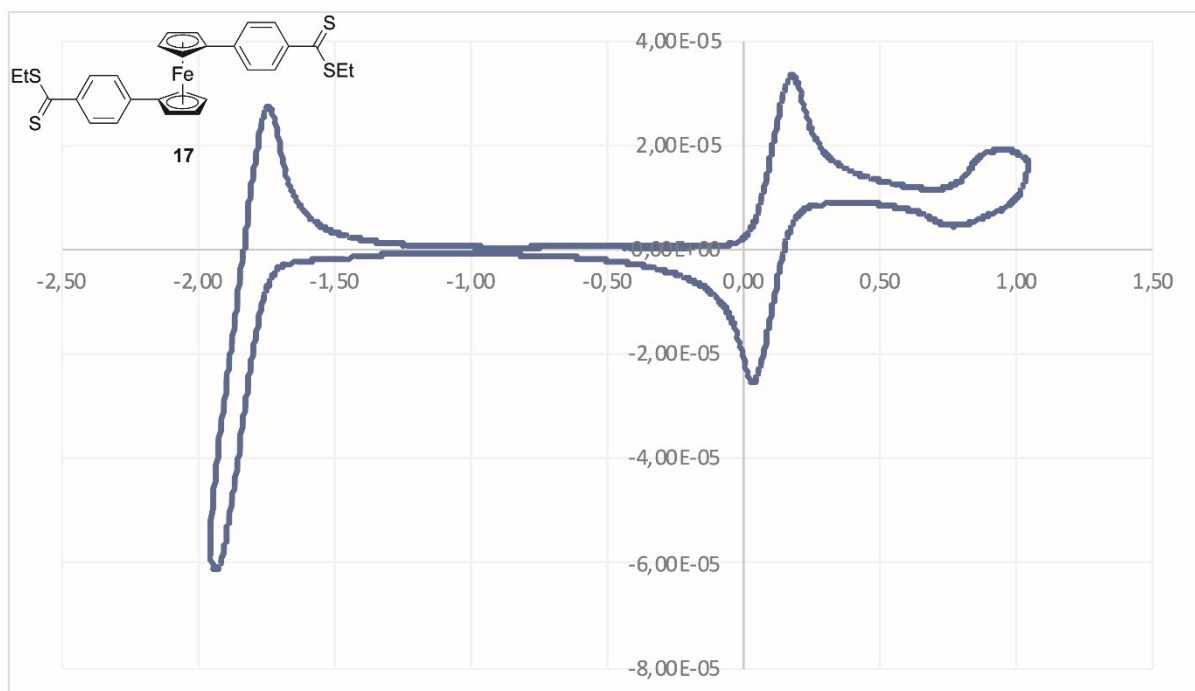
## Experimental Section

**General:** All manipulations involving air-sensitive material were performed in flame-dried reaction vessels in an argon atmosphere by using vacuum-line and standard Schlenk techniques. Diethyl ether, hexane, tetrahydrofuran (THF), and toluene were distilled from sodium benzophenone ketyl. Dichloromethane, chloroform, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were dried with





**Figure 5.** Cyclovoltammogram of **16**. Abscissa: Potential  $U$  [V] vs.  $\text{FcH}/\text{FcH}^+$ , ordinate: Current  $I$  [mA]; scan rate  $\nu = 100$  mV/s;  $c(\text{TBAP}) = 0.1$  mol/L in dichloromethane (TBAP = tetrabutylammonium phosphate),  $c(\mathbf{16}) = 0.005$  mmol/L,  $T = 296$  K.

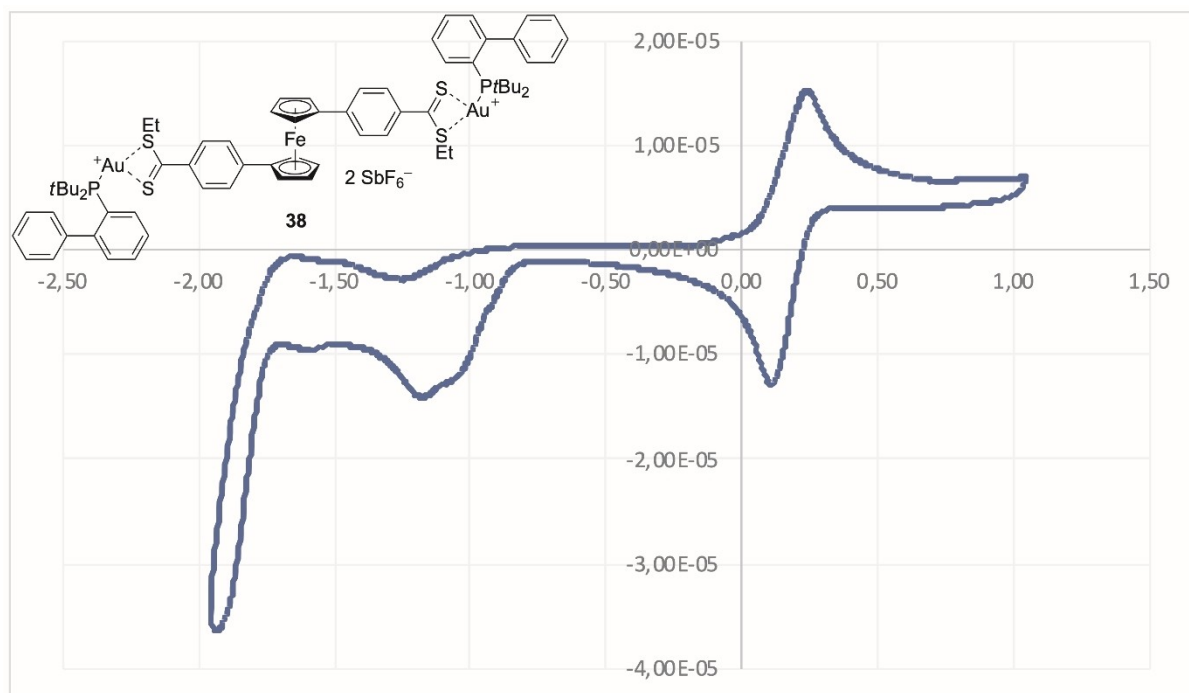


**Figure 6.** Cyclovoltammogram of **17**. Abscissa: Potential  $U$  [V] vs.  $\text{FcH}/\text{FcH}^+$ , ordinate: Current  $I$  [mA]; scan rate  $\nu = 100$  mV/s;  $c(\text{TBAP}) = 0.1$  mol/L in dichloromethane (TBAP = tetrabutylammonium phosphate),  $c(\mathbf{17}) = 0.005$  mmol/L,  $T = 296$  K.

calcium hydride and freshly distilled before use. TMEDA was stored over molecular sieves (4 Å) under argon. Triethylamine and

diisopropylamine were dried over potassium hydroxide and distilled under argon. Petroleum ether was dried with calcium chloride





**Figure 7.** Cyclovoltammogram of **39**. Abscissa: Potential  $U$  [V] vs.  $\text{FcH}/\text{FcH}^+$ , ordinate: Current  $I$  [mA]; scan rate  $\nu = 100$  mV/s;  $c(\text{TBAP}) = 0.1$  mol/L in dichloromethane (TBAP = tetrabutylammonium phosphate),  $c(\mathbf{39}) = 0.005$  mmol/L,  $T = 296$  K.

and distilled. Residual oxygen was removed by Freeze-Pump-Thaw (FTP) cycles as mentioned. **Column chromatography** was carried out by flash chromatography.<sup>[88]</sup> Silica gel (Macherey-Nagel, 40–63  $\mu\text{m}$ , Silica M) was degassed three times by heating it with a flame at reduced pressure followed by setting it under normal pressure with argon. IR: Perkin-Elmer FTIR spectrometer 580 and FT 1170 (ATR). IR: Perkin-Elmer FTIR spectrometer 580 and FT 1170 (ATR). **MS** (ESI): Waters LCT Premier; **HRMS** (EI): Micromass GCT (70 eV). **NMR**: Bruker Ultrashield 400 MHz and Bruker Ascend 400 MHz ( $^1\text{H}$ : 400.1 MHz,  $^{13}\text{C}$ : 100.6 MHz). Signal multiplicities are based on DEPT, COSY, HSQC, and HMBC measurements. **Melting points**: Electrothermal IA 9200 Series Digital Melting Point Apparatus. **Cyclovoltammetry**: Ametek VersaSTAT; substrate (0.005 mmol) in freshly distilled dichloromethane (5 mL); tetrabutylammonium phosphate (194 mg, 0.1 mol/L); scan rate  $\nu = 100$  mV/s; calibration with ferrocene, potentials vs.  $\text{FcH}/\text{FcH}^+$ .

**Dimethyl ferrocene-1,1'-bis(carbodithioate) (10)**: TMEDA (1.1 mL, 6.7 mmol, 2.5 equiv.) was added to ferrocene (**9**, 500 mg, 2.7 mmol, 1.0 equiv.) in hexane (100 mL). At  $-78^\circ\text{C}$  butyllithium (2.5 M in hexane, 3 mL, 6.7 mmol, 2.5 equiv.) was slowly added dropwise. The reaction mixture was stirred for 16 h at  $23^\circ\text{C}$ . After precipitation of the orange solid formed, the solvent was removed by syringe. The solid was washed in hexane ( $2 \times 25$  mL), suspended in diethyl ether (30 mL), and cooled to  $-78^\circ\text{C}$ . Carbon disulfide (0.7 mL, 10.8 mmol, 4.0 equiv.) in diethyl ether (20 mL) was added dropwise. The reaction mixture was stirred for 16 h allowing it to warm from  $-78^\circ\text{C}$  to  $23^\circ\text{C}$ . The mixture was diluted by addition of diethyl ether (10 mL) and cooled to  $-78^\circ\text{C}$ . Iodomethane (0.7 mL, 10.8 mmol, 4.0 equiv.) in diethyl ether (20 mL) was slowly added dropwise. The mixture was stirred for 16 h and allowed to warm from  $-78^\circ\text{C}$  to  $23^\circ\text{C}$ . After the addition of a saturated aqueous ammonium chloride solution (100 mL) the aqueous layer was extracted with diethyl ether ( $2 \times 50$  mL). The collected organic layers were washed with saturated sodium chloride solution, dried over

magnesium sulfate, and filtered. After solvent removal at reduced pressure, the crude product was purified by column chromatography (silica gel deactivated with triethylamine,  $30 \times 3$  cm, petroleum ether  $\rightarrow$  petroleum ether/ethyl acetate, 5:1) giving dimethyl ferrocene-1,1'-bis(carbodithioate) (**10**, 250 mg, 0.7 mmol, 25%) as a dark red viscous oil.

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.70$  (s, 6H,  $\text{CH}_3$ ), 4.54 (m, 4H,  $\text{C}_{\text{Cp}}\text{H}$ ), 5.07 (m, 4H,  $\text{C}_{\text{Cp}}\text{H}$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 19.1$  (s,  $\text{CH}_3$ ), 72.2 (s,  $\text{C}_{\text{Cp}}\text{H}$ ), 75.9 (s,  $\text{C}_{\text{Cp}}\text{H}$ ), 90.5 (s,  $\text{C}_{\text{Cp}}\text{C}$ ), 225.3 (s,  $\text{CS}_2$ ) ppm. IR:  $\tilde{\nu} = 3084$  (w), 2916 (m), 2850 (m), 1654 (w), 1433 (s), 1265 (s), 1074 (s), 1012 (s), 792 (s), 495 (s)  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{14}\text{FeS}_4$  [ $\text{M}^+ + \text{H}$ ] 366.9406, found 366.9408.

**S,S'-Diethyl ferrocene-1,1'-bis(carbothioate) (13)**: Pyridine (4 drops) and oxalyl chloride (0.15 mL, 1.8 mmol, 3.2 equiv.) were added dropwise to ferrocene-1,1'-dicarbocyclic acid<sup>[76]</sup> (**11**, 100 mg, 0.5 mmol, 1.0 equiv.) in dichloromethane (15 mL), and the mixture was heated at reflux ( $45^\circ\text{C}$ ) for 2.5 h. After cooling to  $23^\circ\text{C}$  the solvent was removed at reduced pressure. To the dark red crude ferrocene-1,1'-dicarbonyl dichloride (**12**) ethanethiol (0.1 mL, 1.4 mmol, 2.5 equiv.) and triethylamine (0.3 mL, 2.2 mmol, 4.0 equiv.) in dichloromethane (10 mL) was added dropwise. After stirring for 16 h at  $23^\circ\text{C}$  the mixture was diluted with dichloromethane (15 mL), and half saturated aqueous sodium hydrogen carbonate (40 mL) was added. The aqueous layer was extracted with portions of dichloromethane (40 mL) until it was colorless. The collected organic layers were dried over magnesium sulfate, and after filtration, the solvent was removed at reduced pressure. Purification by column chromatography ( $25 \times 3$  cm, petroleum ether/ethyl acetate 4:1) gave S,S'-diethyl ferrocene-1,1'-bis(carbothioate) (**13**, 183.3 mg, 0.5 mmol, 93%) as an orange solid (m. p.  $53\text{--}55^\circ\text{C}$ ).

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.34$  (t,  $^3J = 7.4$  Hz, 6H,  $\text{CH}_3$ ), 3.02 (q,  $^3J = 7.5$  Hz, 4H,  $\text{CH}_2$ ), 4.46–4.47 (m, 4H,  $\text{C}_{\text{Cp}}\text{H}$ ), 4.87–4.88 (m, 4H,  $\text{C}_{\text{Cp}}\text{H}$ )

ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 15.3$  ( $\text{CH}_3$ ), 23.2 ( $\text{CH}_2$ ), 70.7 ( $\text{C}_{\text{CP}}\text{H}$ ), 74.4 ( $\text{C}_{\text{CP}}\text{H}$ ), 81.3 ( $\text{C}_{\text{CP}}\text{C}$ ), 193.2 ( $\text{C}=\text{O}$ ) ppm. IR:  $\tilde{\nu} = 3093$  (w), 3084 (w), 2983 (w), 2966 (w), 2926 (m), 2868 (w), 1637 (s,  $\text{C}=\text{O}$ ), 1440 (m), 1408 (m), 1365 (m), 1240 (s), 1045 (s), 912 (s), 840 (m), 808 (s), 748 (m), 698 (s), 569 (m), 480 (s)  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}_2\text{FeNa}$  [ $\text{M}^+ + \text{Na}$ ] 384.9993, found 384.9996.

**Diethyl ferrocene-1,1'-bis(carbodithioate) (14):** A solution of *S,S*-diethyl ferrocene-1,1'-bis(carbothioate) (**13**, 75.0 mg, 0.2 mmol, 1.0 equiv.) and Lawesson's reagent (300 mg, 0.8 mmol, 4.0 equiv.) in toluene (15 mL) was heated at reflux (oil bath temperature 120 °C) for 2 h. The solvent was removed at reduced pressure. Column chromatography (20 × 3 cm, petroleum ether/ethyl acetate 2:1) afforded diethyl ferrocene-1,1'-bis(carbodithioate) (**14**, 73.8 mg, 0.2 mmol, 91%) as a deep red oil.

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.36$ –1.38 (br s, 6H,  $\text{CH}_3$ ), 3.32–3.34 (br s, 4H,  $\text{CH}_2$ ), 4.53 (br. s, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 5.06 (br. s, 4H,  $\text{C}_{\text{CP}}\text{H}$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.0$  ( $\text{CH}_3$ ), 29.9 ( $\text{CH}_2$ ), 72.3 ( $\text{C}_{\text{CP}}\text{H}$ ), 76.2 ( $\text{C}_{\text{CP}}\text{H}$ ), 90.4 ( $\text{C}_{\text{CP}}\text{C}$ ), 225.1 ( $\text{C}=\text{S}$ ) ppm. IR:  $\tilde{\nu} = 3101$  (w), 2962 (w), 2922 (m), 2868 (w), 1654 (m), 1433 (s), 1396 (m), 1265 (s), 1240 (m), 1078 (s), 1041 (w), 1008 (s), 931 (m), 823 (s), 790 (s), 657 (w), 499 (s)  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{19}\text{S}_4\text{Fe}$  [ $\text{M}^+ + \text{H}$ ] 394.9719, found 394.9719.

**Diethyl ferrocene-1,1'-di(phenyl-4-carbothioate) (16):** At  $-78^\circ\text{C}$  butyllithium (0.7 mL, 1.7 mmol, 2.5 M in hexane, 2.1 equiv.) was added to 1,1'-di(4-bromophenyl)ferrocene<sup>[65]</sup> (**15**, 400 mg, 0.8 mmol, 1.0 Äq.) in THF (21 mL). After stirring for 30 min an excess of dry ice (8 × 3 g) was added. After stirring for another 30 min at  $-78^\circ\text{C}$  the mixture was allowed to warm to 23 °C. The solvent was removed at reduced pressure, and the remaining orange solid was dissolved in chloroform (50 mL). Pyridine (4 drops), oxalyl chloride (0.22 mL, 2.6 mmol, 3.2 equiv.), and *N,N*-dimethylformamide (1 mL, for better solubility) were added dropwise, and the mixture was heated at reflux for 2.5 h (oil bath temperature 75 °C). After cooling to 23 °C the solvent was removed at reduced pressure, and the dark red residue was taken up in chloroform (30 mL). Ethanethiol (0.15 mL, 2.0 mmol, 2.5 equiv.) and triethylamine (0.9 mL, 6.5 mmol, 8.0 equiv.) in chloroform (13 mL) were added dropwise. After stirring for 16 h at 23 °C the mixture was diluted by addition of dichloromethane (20 mL), and the reaction was stopped by addition of half saturated aqueous sodium hydrogen carbonate (50 mL). The aqueous layer was extracted with portions of dichloromethane (25 mL) until it was colorless. The collected organic layers were dried over magnesium sulfate, after filtration the solvent was removed at reduced pressure. Purification by column chromatography (25 × 3 cm, petroleum ether/ethyl acetate 6:1) afforded diethyl ferrocene-1,1'-di(phenyl-4-carbothioate) (**16**, 260 mg, 0.5 mmol, 62%) as a red solid (m. p. 122–130 °C, dec.).

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.37$  (t,  $^3J = 7.4$  Hz, 6H,  $\text{CH}_3$ ), 3.08 (q,  $^3J = 7.4$  Hz, 4H,  $\text{CH}_2$ ), 4.31–4.32 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 4.54–4.55 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 7.23–7.25 + 7.74–7.76 (AA'BB', 2 × 4H,  $\text{C}_{\text{PH}}\text{H}$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 15.0$  ( $\text{CH}_3$ ), 23.5 ( $\text{CH}_2$ ), 68.5 ( $\text{C}_{\text{CP}}\text{H}$ ), 71.6 ( $\text{C}_{\text{CP}}\text{H}$ ), 84.5 ( $\text{C}_{\text{CP}}\text{C}$ ), 125.0 ( $\text{C}_{\text{PH}}\text{H}$ ), 127.4 ( $\text{C}_{\text{PH}}\text{H}$ ), 134.7 ( $\text{C}_{\text{PH}}\text{CC}$ ), 143.7 ( $\text{C}_{\text{PH}}\text{C}=\text{O}$ ), 191.4 ( $\text{C}=\text{O}$ ) ppm. IR:  $\tilde{\nu} = 2924$  (w), 1654 (s,  $\text{C}=\text{O}$ ), 1600 (s), 1564 (w), 1521 (w), 1454 (m), 1415 (m), 1215 (m), 1174 (s), 1111 (w), 1082 (m), 1037 (m), 916 (s), 885 (s), 840 (s), 813 (s), 740 (m), 715 (s), 648 (s)  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{26}\text{O}_2\text{S}_2\text{Fe}$  [ $\text{M}^+$ ] 514.0724, found 514.0727.

Crystal structure analysis of **16**.<sup>[79]</sup> Single crystals (orange needles) of **16** were obtained by slow diffusion of dichloromethane/hexane. Empirical formula  $\text{C}_{28}\text{H}_{26}\text{FeO}_2\text{S}_2$ , formula weight 514.46 g/mol, crystal system monoclinic, space group  $\text{P}1_21/c1$ , unit cell dimensions  $a = 8.7992(18)$ ,  $b = 10.444(2)$ ,  $c = 26.084(5)$  Å,  $\alpha = 90.00^\circ$ ,  $\beta = 97.900(7)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 2374.4(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd.}} = 1.439$  g/

$\text{cm}^3$ ,  $\mu = 0.835$  mm<sup>-1</sup>, crystal size 0.64 × 0.60 × 0.40 mm<sup>3</sup>,  $F(000) = 1072$ , Bruker SMART X2S,  $T = 200(2)$  K, Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å),  $\theta$ -range 2.337–29.194°, reflections collected/unique 24230/6215, parameters/restraints 340/39, index ranges  $-11 \leq h \leq 11$ ,  $-14 \leq k \leq 13$ ,  $-35 \leq l \leq 20$ , multi-scan absorption correction (SADABS), no extinction correction, structure resolution and refinement OLEX2 (Dolomanov, 2009) SHELXT and SHELXL-2018/3 (Sheldrick, 2015),<sup>[89,90]</sup> full-matrix least-squares refinement on  $F^2$ , goodness-of-fit on  $F^2 = 1.007$ ,  $R_1 = 0.0672$  ( $I > 2\sigma$ ),  $wR_2 = 0.1855$  (all data), final difference electron density 0.435 and  $-0.417$  eÅ<sup>-3</sup>.

**Diethyl ferrocene-1,1'-bis(phenyl-4-carbodithioate) (17):** A solution of diethyl ferrocene-1,1'-di(phenyl-4-carbothioate) (**16**, 64 mg, 0.1 mmol, 1.0 equiv.) and Lawesson's reagent (200 mg, 0.5 mmol, 4.0 equiv.) in toluene (14 mL) was stirred for 16 h at 100 °C. The solvent was removed at reduced pressure. Column chromatography (neutral  $\text{Al}_2\text{O}_3$ , 23 × 3 cm, petroleum ether/dichloromethane 1:1) afforded diethyl ferrocene-1,1'-di(phenyl-4-carbodithioate) (**17**, 62 mg, 0.1 mmol, 91%) as a deep red solid (m. p. 97–103 °C, dec.).

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.43$  (t,  $^3J = 7.4$  Hz, 6H,  $\text{CH}_3$ ), 3.37 (q,  $^3J = 7.4$  Hz, 4H,  $\text{CH}_2$ ), 4.33–4.34 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 4.57–4.58 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 7.15–7.17 + 7.82–7.84 (AA'BB', 2 × 4H,  $\text{C}_{\text{PH}}\text{H}$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 12.6$  ( $\text{CH}_3$ ), 31.4 ( $\text{CH}_2$ ), 68.3 ( $\text{C}_{\text{CP}}\text{H}$ ), 71.5 ( $\text{C}_{\text{CP}}\text{H}$ ), 84.6 ( $\text{C}_{\text{CP}}\text{C}$ ), 125.3 ( $\text{C}_{\text{PH}}\text{H}$ ), 127.2 ( $\text{C}_{\text{PH}}\text{H}$ ), 142.5 ( $\text{C}_{\text{PH}}\text{CC}$ ), 142.8 ( $\text{C}_{\text{PH}}\text{C}=\text{S}$ ), 226.9 ( $\text{C}=\text{S}$ ) ppm. IR:  $\tilde{\nu} = 2964$  (w), 2920 (w), 2850 (w), 1595 (s), 1500 (m), 1410 (m), 1259 (s), 1238 (s), 1184 (s), 1120 (m), 1083 (m), 1031 (s), 916 (m), 829 (m), 815 (s), 763 (m)  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{26}\text{S}_4\text{Fe}$  [ $\text{M}^+$ ] 546.0267, found 546.0266.

***S,S*-Diethyl ferrocene-1,1'-di(2-thienyl-4-carbothioate) (19):** At  $-78^\circ\text{C}$  butyllithium (2.5 M in hexane, 0.7 mL, 1.8 mmol, 2.1 equiv.) was added to 1,1'-di(2-thienyl)ferrocene (**18**, 300 mg, 0.9 mmol, 1.0 equiv.) in THF (16 mL), and the mixture was stirred for 30 min. Then an excess of dry ice (8 portions) was added, and stirring was continued for 30 min. After warming to 23 °C the solvent was removed at reduced pressure. The obtained orange solid was dissolved in chloroform (40 mL), and pyridine (4 drops), oxalyl chloride (0.24 mL, 2.8 mmol, 3.2 equiv.), and *N,N*-dimethylformamide (1 mL, for better solubility) were added dropwise, and the mixture was heated at reflux for 2.5 h (oil bath temperature 75 °C). After cooling to 23 °C the solvent was removed at reduced pressure, and the dark red residue was taken up in chloroform (20 mL), and ethanethiol (0.16 mL, 2.1 mmol, 2.5 equiv.) and triethylamine (0.95 mL, 6.9 mmol, 8.0 equiv.) in chloroform (10 mL) were added dropwise. After stirring for 16 h at 23 °C the mixture was diluted by addition of dichloromethane (20 mL), and the reaction was terminated by addition of half saturated aqueous sodium hydrogen carbonate (40 mL). The aqueous layer was extracted with dichloromethane (portions of 30 mL) until it remained colorless. After drying the collected organic layers with magnesium sulfate and filtration the solvent was removed at reduced pressure. Purification by column chromatography (30 × 3 cm, petroleum ether/ethyl acetate 2:1) afforded *S,S*-diethyl ferrocene-1,1'-di(2-thienyl-4-carbothioate) (**19**, 230 mg, 0.4 mmol, 51%) as a red solid (m. p. 117–121, dec.).

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.37$  (t,  $^3J = 7.4$  Hz, 6H,  $\text{CH}_3$ ), 3.08 (q,  $^3J = 7.4$  Hz, 4H,  $\text{CH}_2$ ), 4.32–4.33 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 4.55–4.56 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 6.74–6.75 (d,  $^3J = 4.0$  Hz, 2H,  $\text{SC}=\text{CH}$ ), 7.48–7.49 (d,  $^3J = 4.0$  Hz, 2H,  $\text{SC}=\text{CH}$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 15.1$  ( $\text{CH}_3$ ), 23.7 ( $\text{CH}_2$ ), 69.0 ( $\text{C}_{\text{CP}}\text{H}$ ), 71.7 ( $\text{C}_{\text{CP}}\text{H}$ ), 80.2 ( $\text{C}_{\text{CP}}\text{C}$ ), 123.3 (SCCH), 131.8 (SCCH), 139.0 (SCC<sub>CP</sub>), 149.8 (CC=O), 183.5 (C=O) ppm. IR:  $\tilde{\nu} = 3093$  (w), 2929 (w), 2870 (w), 1654 (w), 1620 (s,  $\text{C}=\text{O}$ ), 1535 (m), 1477 (m), 1417 (m), 1348 (w), 1255 (m), 1209 (s), 1072 (m), 1049 (m), 1033 (m), 979 (w), 862 (m), 819 (s), 802 (s), 694 (w), 657 (s)  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{22}\text{FeO}_2\text{S}_4\text{Na}$  [ $\text{M} + \text{Na}^+$ ] 548.9750, found 548.9749.

Crystal structure analysis of **19**:<sup>[79]</sup> Single crystals (red plates) of **19** were obtained by slow diffusion of dichloromethane/hexane. Empirical formula  $C_{24}H_{22}FeO_2S_4$ , formula weight 526.50 g/mol, crystal system triclinic, space group *P*-1, unit cell dimensions  $a = 9.9828(5)$ ,  $b = 10.8793(6)$ ,  $c = 11.1679(6)$  Å,  $\alpha = 104.386(4)^\circ$ ,  $\beta = 90.687(3)^\circ$ ,  $\gamma = 107.406(4)^\circ$ ,  $V = 1116.17$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calc}} = 1.567$  g/cm<sup>3</sup>,  $\mu = 9.077$  mm<sup>-1</sup>, crystal size  $0.25 \times 0.23 \times 0.22$  mm<sup>3</sup>,  $F(000) = 544$ , Bruker Apex-II CCD,  $T = 233.15(2)$  K, Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å),  $\theta$ -range  $4.41$ – $65.93^\circ$ , reflections collected/unique 10867/3679, parameters/restraints 282/0, completeness of data  $q = 25.17$  (95%), index ranges  $-9 \leq h \leq 11$ ,  $-12 \leq k \leq 11$ ,  $-13 \leq l \leq 12$ , multi-scan absorption correction (SADABS), no extinction correction, structure resolution ShelXS (Sheldrick, 2008)<sup>[91]</sup> and refinement SHELXL-2014/7 (Sheldrick, 2014),<sup>[92]</sup> full-matrix least-squares refinement on  $F^2$ , goodness-of-fit on  $F^2 = 1.070$ ,  $R_1 = 0.0584$  ( $I > 2\sigma$ ),  $wR_2 = 0.1796$  (all data), final difference electron density 0.735 and  $-0.616$  eÅ<sup>-3</sup>.

**Diethyl ferrocene-1,1'-bis(2-thienyl-4-carbodithioate) (20)**: A solution of diethyl diethyl ferrocene-1,1'-di(2-thienyl-4-carbodithioate) (**19**, 231 mg, 0.4 mmol, 1.0 equiv.) and Lawesson's reagent (700 mg, 1.8 mmol, 4.0 equiv.) in toluene (40 mL) was stirred for 16 h at 100 °C. The solvent was removed at reduced pressure. Column chromatography (neutral Al<sub>2</sub>O<sub>3</sub>, 17×3 cm, petroleum ether/dichloromethane 1:2) afforded diethyl ferrocene-1,1'-di(2-thienyl-4-carbodithioate) (**20**, 230 mg, 0.4 mmol, 94%) as a black solid (m. p. 109–111 °C, dec.).

<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.41$  (t,  $^3J = 7.4$  Hz, 6H, CH<sub>3</sub>), 3.37 (q,  $^3J = 7.4$  Hz, 4H, CH<sub>2</sub>), 4.37–4.38 (m, 4H, C<sub>cp</sub>H), 4.59–4.60 (m, 4H, C<sub>cp</sub>H), 6.76 (d,  $^3J = 4.1$  Hz, 2H, CCCH), 7.49 (d,  $^3J = 4.1$  Hz, 2H, SCCH) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 13.1$  (CH<sub>3</sub>), 30.6 (CH<sub>2</sub>), 68.8 (C<sub>cp</sub>H), 71.8 (C<sub>cp</sub>H), 80.6 (C<sub>cp</sub>C), 124.4 (SCCH), 127.6 (SCCH), 148.9 (SCC<sub>cp</sub>), 152.3 (CC=S), 211.7 (C=S) ppm. IR:  $\tilde{\nu} = 3074$  (w), 2964 (w), 2924 (w), 2852 (w), 2366 (w), 2326 (w), 1716 (w), 1462 (s), 1413 (s), 1346 (m), 1317 (m), 1261 (s), 1240 (m), 1180 (w), 1072 (w), 1033 (s), 860 (m), 796 (s), 655 (m) cm<sup>-1</sup>. HRMS (ESI):  $m/z$  calcd. for C<sub>24</sub>H<sub>22</sub>FeS<sub>6</sub> [M<sup>+</sup>] 557.9395, found 557.9385.

**Dimethyl 4,4'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]dibenzoate (24)**: A solution of 1,1'-diiodoferrocene<sup>[82,93]</sup> (**22**, 570 mg, 1.3 mmol, 1.0 equiv.), methyl 4-ethynylbenzoate (**23**, 450 mg, 2.8 mmol, 2.2 equiv.), bis(tri-*tert*-butylphosphane)palladium(0) (40.9 mg, 0.08 mmol, 0.06 equiv.) and copper(I) iodide (17.8 mg, 0.09 mmol, 0.07 equiv.) in THF/diisopropylamine (3:1, 8 mL) was stirred for 16 h at 23 °C. After solvent removal at reduced pressure the product was purified by column chromatography (20×5 cm, petroleum ether/dichloromethane 1:3) affording dimethyl 4,4'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]dibenzoate (**24**, 600 mg, 1.2 mmol, 96%) as an orange solid (m. p. 106–111 °C).

<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 3.92$  (s, 6H, OCH<sub>3</sub>), 4.35–4.36 (m, 4H, C<sub>cp</sub>H), 4.57–4.58 (m, 4H, C<sub>cp</sub>H), 7.38–7.40 + 7.84–7.86 (AA'BB', 2×4H, C<sub>ph</sub>H) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 52.3$  (OCH<sub>3</sub>), 67.0 (C<sub>cp</sub>C), 71.2 (C<sub>cp</sub>H), 73.2 (C<sub>cp</sub>H), 86.6 (C<sub>cp</sub>C≡CC<sub>ph</sub>), 90.5 (C<sub>cp</sub>C≡CC<sub>ph</sub>), 128.6 (C<sub>ph</sub>C=O), 128.8 (C≡CC<sub>ph</sub>), 129.5 (C<sub>ph</sub>H), 131.2 (C<sub>ph</sub>H), 166.7 (C=O) ppm. IR:  $\tilde{\nu} = 2990$  (w), 2940 (w), 2880 (w), 2208 (w), 1712 (s, C=O), 1602 (m), 1431 (m), 1406 (w), 1307 (w), 1276 (s), 1163 (m), 1109 (m), 1016 (m), 968 (w), 765 (m), 692 (w) cm<sup>-1</sup>. HRMS (ESI):  $m/z$  calcd. for C<sub>30</sub>H<sub>22</sub>FeO<sub>4</sub>Na [M + Na<sup>+</sup>] 525.0765, found 525.0767.

**S,S-Diethyl 4,4'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]dibenzothioate (25)**: At 0 °C ethanethiol (0.06 mL, 0.8 mmol, 4.0 equiv.) was slowly added dropwise to trimethylaluminum (2 M in hexane, 0.4 mL, 0.8 mmol, 4.0 equiv.) in dichloromethane (1 mL). The mixture was stirred for 15 min at 0 °C and then added dropwise to dimethyl 4,4'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]dibenzoate (**24**, 100 mg, 0.2 mmol, 1.0 equiv.) in dichloromethane (3 mL). After stirring for 2 h at 23 °C diethyl ether (5 mL) was added, and the

mixture was washed with aqueous hydrochloric acid (3%, 10 mL). The aqueous layer was extracted with diethyl ether (10 mL). The organic layer was washed with aqueous sodium hydroxide (5%, 3×10 mL). The collected organic layers were dried over magnesium sulfate and filtered, then the solvent was removed at reduced pressure. Column chromatography (16×4 cm, petroleum ether/dichloromethane 1:2) afforded S,S-Dimethyl 4,4'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]dibenzothioate (**25**, 100 mg, 0.18 mmol, 90%) as an orange solid (m. p. 161–164 °C).

<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.36$  (t,  $^3J = 7.4$  Hz, 6H, CH<sub>3</sub>), 3.07 (q,  $^3J = 7.4$  Hz, 4H, CH<sub>2</sub>), 4.36–4.37 (m, 4H, C<sub>cp</sub>H), 4.58–4.59 (m, 4H, C<sub>cp</sub>H), 7.39–7.41 + 7.79–7.81 (AA'BB', 2×4H, C<sub>ph</sub>H) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 14.9$  (CH<sub>3</sub>), 23.7 (CH<sub>2</sub>), 66.9 (C<sub>cp</sub>C), 71.3 (C<sub>cp</sub>H), 73.3 (C<sub>cp</sub>H), 86.6 (C<sub>cp</sub>C≡CC<sub>ph</sub>), 91.0 (C<sub>cp</sub>C≡CC<sub>ph</sub>), 127.1 (C<sub>ph</sub>H), 129.0 (C≡CC<sub>ph</sub>), 131.4 (C<sub>ph</sub>H), 135.8 (C<sub>ph</sub>C=O), 191.3 (C=O) ppm. IR:  $\tilde{\nu} = 3100$  (w), 2990 (w), 2910 (w), 2206 (m), 1654 (s, C=O), 1597 (s), 1390 (w), 1207 (s), 1180 (m), 1157 (s), 1040 (w), 912 (s), 821 (m), 790 (m), 644 (m) cm<sup>-1</sup>. HRMS (ESI):  $m/z$  calcd. for C<sub>32</sub>H<sub>26</sub>FeO<sub>2</sub>S<sub>2</sub> [M<sup>+</sup>] 562.0724, found 562.0723.

**S,S-Dibenzyl 4,4'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]dibenzothioate (26)**: At 0 °C benzylthiol (0.05 mL, 0.4 mmol, 4.0 equiv.) was slowly added dropwise to trimethylaluminum (2 M in hexane, 0.2 mL, 0.4 mmol, 4.0 equiv.) in dichloromethane (0.5 mL). The mixture was stirred for 15 min at 0 °C and then added dropwise to dimethyl 4,4'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]dibenzoate (**24**, 50 mg, 0.1 mmol, 1.0 equiv.) in dichloromethane (1.5 mL). After stirring for 2 h at 23 °C diethyl ether (3 mL) was added, and the mixture was washed with aqueous hydrochloric acid (3%, 5 mL). The aqueous layer was extracted with diethyl ether (5 mL). The organic layer was washed with aqueous sodium hydroxide (5%, 3×5 mL). The collected organic layers were dried over magnesium sulfate and filtered, then the solvent was removed at reduced pressure. Column chromatography (15×3 cm, petroleum ether/dichloromethane 1:2) afforded S,S-Dibenzyl 4,4'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]dibenzothioate (**26**, 58.2 mg, 0.08 mmol, 85%) as an orange solid (m. p. 159–163 °C).

<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 4.29$  (s, 4H, CH<sub>2</sub>), 4.36–4.37 (m, 4H, C<sub>cp</sub>H), 4.57–4.58 (m, 4H, C<sub>cp</sub>H), 7.27–7.28 (m, 2H, C<sub>ph</sub>H), 7.30–7.34 (m, 4H, C<sub>ph</sub>H), 7.37–7.40 (m, 8H, C<sub>ph</sub>H), 7.80–7.82 (m, 4H, C<sub>ph</sub>H) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 33.6$  (CH<sub>2</sub>), 68.8 (C<sub>cp</sub>C), 71.3 (C<sub>cp</sub>H), 73.3 (C<sub>cp</sub>H), 86.5 (C<sub>ph</sub>C≡C), 91.3 (C<sub>ph</sub>C≡C), 127.3 (C<sub>6</sub>H<sub>4</sub>), 127.5 (C<sub>ph</sub>H), 128.8 (C<sub>ph</sub>H), 129.1 (C<sub>ph</sub>H), 129.2 (C≡CC<sub>ph</sub>), 131.4 (C<sub>ph</sub>H), 135.4 (C<sub>ph</sub>C=O), 137.5 (CH<sub>2</sub>C<sub>ph</sub>), 190.5 (C=O) ppm. IR:  $\tilde{\nu} = 3084$  (w), 3061 (w), 3026 (w), 2929 (w), 2202 (m), 1651 (s, C=O), 1597 (s), 1494 (m), 1452 (m), 1404 (m), 1303 (w), 1282 (w), 1209 (s), 1176 (m), 1157 (s), 1109 (w), 1028 (m), 914 (s), 829 (s), 696 (s), 638 (s), 549 (w) cm<sup>-1</sup>. HRMS (ESI):  $m/z$  calcd. for C<sub>42</sub>H<sub>30</sub>FeO<sub>2</sub>S<sub>2</sub> [M<sup>+</sup>] 686.1037, found 686.1026.

**1,1'-Di[(2-thienyl)ethynyl]ferrocene (29)**: A solution of 1,1'-diiodoferrocene<sup>[82,93]</sup> (**22**, 700 mg, 1.7 mmol, 1.0 equiv.), 2-ethynylthiophene (**28**, 400 mg, 0.36 mL, 3.7 mmol, 2.2 equiv.),<sup>[94]</sup> bis(tri-*tert*-butylphosphane)palladium(0) (65.4 mg, 0.1 mmol, 0.06 equiv.) and copper(I) iodide (22.6 mg, 0.12 mmol, 0.07 equiv.) in THF/diisopropylamine (3:1, 10 mL) was stirred for 16 h at 23 °C. After solvent removal at reduced pressure the product was purified by column chromatography (20×4 cm, petroleum ether/dichloromethane 4:1) affording 1,1'-di[(2-thienyl)ethynyl]ferrocene (**29**, 600 mg, 1.5 mmol, 91%) as a red solid (m. p. 111–116 °C, dec.).

<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 4.33$ – $4.34$  (m, 4H, C<sub>cp</sub>H), 4.54–4.55 (m, 4H, C<sub>cp</sub>H), 6.94 (dd,  $^3J = 5.2$  Hz, 2H, SCCH), 7.16 (dd,  $^3J = 3.6$  Hz, 2H, SCCH), 7.21 (dd,  $J = 5.2$ , 3.6 Hz, 2H, SCH) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 66.7$  (C<sub>cp</sub>C), 71.4 (C<sub>cp</sub>H), 73.0 (C<sub>cp</sub>H), 79.8 (C<sub>cp</sub>C≡C), 91.2 (C<sub>cp</sub>C≡C), 124.1 (C≡CCS), 126.6 (SCHCH or SCCH),

127.1 (SCHCH or SCCH), 131.5 (SCCH) ppm. IR:  $\tilde{\nu}$  = 3100 (w), 2900 (w), 2340 (w), 1525 (w), 1413 (w), 1217 (m), 1124 (m), 1043 (w), 1024 (m), 920 (m), 848 (m), 815 (s), 694 (s), 491 (s)  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{14}\text{FeS}_2$  [ $\text{M}^+$ ]: 397.9886, found 397.9885.

***S,S'*-Diethyl 5,5'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]bis(thiophene-2-carbothioate) (30)**: At  $-78^\circ\text{C}$  butyllithium (2.5 M in hexane, 0.3 mL, 0.8 mmol, 2.1 equiv.) was added to 1,1'-di[(2-thienyl)ethynyl]ferrocene (**29**, 150 mg, 0.4 mmol, 1.0 equiv.) in THF (10 mL), and the mixture was stirred for 30 min. Then an excess of dry ice (8 portions) was added, and stirring was continued for 30 min. After slow warming to  $23^\circ\text{C}$ , the solvent was removed at reduced pressure. The obtained orange solid was dissolved in chloroform (40 mL), and pyridine (4 drops), oxalyl chloride (0.1 mL, 1.2 mmol, 3.2 equiv.), and *N,N*-dimethylformamide (0.3 mL, for better solubility) were added dropwise, and the mixture was heated at reflux for 2.5 h (oil bath temperature  $75^\circ\text{C}$ ). After cooling to  $23^\circ\text{C}$  the solvent was removed at reduced pressure, and the dark red residue was taken up in chloroform (20 mL), and ethanethiol (0.7 mL, 0.9 mmol, 2.5 equiv.) and triethylamine (0.4 mL, 3.0 mmol, 8.0 equiv.) in chloroform (10 mL) were added dropwise. After stirring for 16 h at  $23^\circ\text{C}$  the mixture was diluted by addition of dichloromethane (20 mL), and the reaction was terminated by addition of half saturated aqueous sodium hydrogen carbonate (40 mL). The aqueous layer was extracted with dichloromethane (portions of 30 mL) until it remained colorless. After drying the collected organic layers with magnesium sulfate and filtration the solvent was removed at reduced pressure. Purification by column chromatography (25  $\times$  3 cm, petroleum ether/dichloromethane 1:1.5) afforded *S,S'*-diethyl 5,5'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]bis(thiophene-2-carbothioate) (**30**, 93.4 mg, 0.16 mmol, 43%) as a red solid (m. p. 109–113, dec.).

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.36 (t,  $^3J$  = 7.4 Hz, 6H,  $\text{CH}_3$ ), 3.07 (q,  $^3J$  = 7.4 Hz, 4H,  $\text{CH}_2$ ), 4.37–4.38 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 4.58–4.59 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 7.01–7.02 (d,  $^3J$  = 4.0 Hz, 2H, SCCH), 7.54–7.55 (d,  $^3J$  = 4.0 Hz, 2H, SCCH) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 15.0 ( $\text{CH}_3$ ), 23.9 ( $\text{CH}_2$ ), 66.5 ( $\text{C}_{\text{CP}}\text{C}$ ), 71.4 ( $\text{C}_{\text{CP}}\text{H}$ ), 73.2 ( $\text{C}_{\text{CP}}\text{H}$ ), 80.0 ( $\text{C}_{\text{CP}}\text{C}\equiv\text{C}$ ), 95.1 ( $\text{C}_{\text{CP}}\text{C}\equiv\text{C}$ ), 130.7 (SCCH), 131.7 (SCCH), 131.6 (SCCH), 141.5 (SCCH), 183.4 ( $\text{C}=\text{O}$ ) ppm. IR:  $\tilde{\nu}$  = 2964 (w), 2926 (w), 2870 (w), 2210 (w), 2187 (w), 1676 (w), 1625 (s,  $\text{C}=\text{O}$ ), 1479 (m), 1421 (s), 1390 (w), 1273 (w), 1205 (s), 1049 (m), 1028 (s), 921 (w), 840 (s), 804 (s), 657 (m), 543 (w), 503 (m)  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{22}\text{FeO}_2\text{S}_4\text{Na}$  [ $\text{M} + \text{Na}^+$ ] 596.9750, found 596.9746.

**Reaction of 30 with Lawesson's Reagent**: *S,S'*-Diethyl 5,5'-[1,1'-ferrocenylenebis(ethyne-2,1-diyl)]bis(thiophene-2-carbothioate) (**30**, 91 mg, 0.15 mmol, 1.0 equiv.) and Lawesson's reagent (240 mg, 0.6 mmol, 4.0 equiv.) in toluene (18 mL) were stirred for 16 h at  $100^\circ\text{C}$ . After solvent removal at reduced pressure the mixture was separated by column chromatography (neutral alumina, 20  $\times$  3 cm, petroleum ether/dichloromethane 1:2). **32** or **33** (15 mg, 9%) was obtained as a deep red solid (m. p. 136.6  $^\circ\text{C}$ ).

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.37 (t,  $^3J$  = 5.9 Hz, 6H,  $\text{CH}_2\text{CH}_3$ ), 3.32 (q,  $^3J$  = 5.9 Hz, 4H,  $\text{CH}_2\text{CH}_3$ ), 3.85 (s, 6H,  $\text{OCH}_3$ ), 4.29, (m, 2H,  $\text{C}_{\text{FC}}\text{H}$ ), 4.61 (m, 4H,  $\text{C}_{\text{FC}}\text{H}$ ), 4.72 (m, 2H,  $\text{C}_{\text{FC}}\text{H}$ ), 6.89 (dd, 2H,  $^3J$  = 3.2 Hz,  $J$  = 1.6 Hz, SCCH), 6.94 + 7.98 (AA'BB', 4 + 4H, PCCH, PCCH), 7.54 (dd, 2H,  $^3J$  = 3.2 Hz,  $J$  = 0.4 Hz, SCCH). 212.8 ( $\text{C}=\text{S}$ ) ppm  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 12.8 ( $\text{CH}_2\text{CH}_3$ ), 30.4 ( $\text{CH}_2\text{CH}_3$ ), 55.5 ( $\text{OCH}_3$ ), 72.0 ( $\text{C}_{\text{FC}}\text{H}$ ), 72.3 ( $\text{C}_{\text{FC}}\text{H}$ ), 73.2 ( $\text{C}_{\text{FC}}\text{H}$ ), 75.7 ( $\text{C}_{\text{FC}}\text{H}$ ), 114.1 (PCCHCH), 126.8 (SCCH), 129.4 (SCCH), 135.0 (PCCH) ppm (5 quaternary C signals could not be detected).  $^{31}\text{P}$  NMR (162.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 93.63 ppm. IR:  $\tilde{\nu}$  = 2922 (m), 1589 (s), 1564 (m), 1494 (s), 1434 (m), 1418 (s), 1327 (m), 1306 (m), 1294 (m), 1256 (s), 1231 (s), 1176 (s), 1098 (s), 1059 (s), 1024 (s), 995 (m), 907 (m), 827 (m), 800 (s), 743 (m), 685 (s), 615 (s), 526 (m), 486 (s), 416 (m)  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{42}\text{H}_{36}\text{FeO}_2\text{P}_2\text{S}_{12}$  [ $\text{M}^+$ ] 1073.8188, found 1073.8198.

**Gold Complex 39**: At  $23^\circ\text{C}$  (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphane]gold(I) hexafluoroantimonate(V) [JohnphosAu(MeCN)SbF<sub>6</sub>, **37**]<sup>[87]</sup> (50.9 mg, 0.07 mmol, 1.8 equiv.) was added to diethyl ferrocene-1,1'-di(phenyl-4-carbodithioate) (**17**, 20.0 mg, 0.04 mmol, 1.0 equiv.) in dichloromethane (5 mL). After stirring for 10 min the solvent was removed at reduced pressure, and the residue was washed with pentane (5  $\times$  5 mL). Gold complex **39** (66.1 mg, 0.03 mmol, 90%) was obtained as a turquoise solid (m. p. 228–232  $^\circ\text{C}$ , dec.).

$\text{C}_{\text{Ar}}$  refers to phosphane aryl carbon atoms.  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.17 [d,  $^3J_{\text{P,H}}$  = 16 Hz, 36H,  $\text{C}(\text{CH}_3)_3$ ], 1.62 (t,  $^3J_{\text{H,H}}$  = 7.4 Hz, 6H,  $\text{CH}_2\text{CH}_3$ ), 3.50 (q,  $^3J_{\text{H,H}}$  = 7.5 Hz, 4H,  $\text{CH}_2$ ), 4.65 (very br. s, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 5.03 (very br. s, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 6.98 + 7.37–7.38 (AA'BB', 2  $\times$  4H,  $\text{FcC}_6\text{H}_4$ ), 7.16–7.17 (m, 4H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.25 (br. s, 2H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.47–7.49 (m, 8H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.51–7.54 (t,  $^3J_{\text{H,H}}$  = 7.5 Hz, 2H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.75–7.78 (t,  $^3J_{\text{H,H}}$  = 7.8 Hz, 2H,  $\text{C}_{\text{Ar}}\text{H}$ ) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 12.3 ( $\text{CH}_2\text{CH}_3$ ), 30.7 [d,  $^2J_{\text{P,C}}$  = 6.3 Hz,  $\text{PC}(\text{CH}_3)_3$ ], 35.2 ( $\text{CH}_2$ ), 38.2 (d,  $^1J_{\text{P,C}}$  = 23.5 Hz,  $\text{PC}(\text{CH}_3)_3$ ), 125.2 (d,  $^1J_{\text{P,C}}$  = 45.1 Hz,  $\text{PC}_{\text{Ar}}$ ), 126.2 (FcCCH or FcCCHCH), 127.5 (d,  $^2J_{\text{P,C}}$  = 6.9 Hz,  $\text{PC}_{\text{Ar}}\text{C}_{\text{Ar}}\text{H}$ ), 128.0 (FcCCH or FcCCHCH), 128.2 (FcCCHCHCC=S), 129.2 ( $\text{C}_{\text{Ar}}\text{H}$ ), 130.0 ( $\text{C}_{\text{Ar}}\text{H}$ ), 131.3 (d,  $J_{\text{P,C}}$  = 2.3 Hz,  $\text{C}_{\text{Ar}}\text{H}$ ), 133.4 (d,  $^3J_{\text{P,C}}$  = 5.1 Hz,  $\text{C}_{\text{Ar}}\text{H}$ ), 133.5 ( $\text{C}_{\text{Ar}}\text{H}$ ), 142.9 (d,  $^3J_{\text{P,C}}$  = 6.7 Hz,  $\text{PC}_{\text{Ar}}\text{C}_{\text{Ar}}\text{C}_{\text{Ar}}\text{H}$ ), 145.8 ( $\text{C}_{\text{FC}}\text{CCH}$ ), 149.2 (d,  $^2J_{\text{P,C}}$  = 13.4 Hz,  $\text{PC}_{\text{Ar}}\text{C}_{\text{Ar}}\text{C}_{\text{Ar}}\text{H}$ ), 235.8 ( $\text{C}=\text{S}$ ) ppm. Presumably due to coalescence, cyclopentadienyl carbon atom signals are not observed (*cf.*  $^1\text{H}$  NMR signals at  $\delta$  = 4.65, 5.03 ppm); due to signal overlap one phosphane ligand  $\text{C}_{\text{Ar}}\text{H}$  is not observed.  $^{31}\text{P}$  NMR (162.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 64.28 ppm. IR:  $\tilde{\nu}$  = 2953 (w), 2926 (w), 2870 (w), 1591 (m), 1462 (w), 1369 (w), 1253 (m), 1188 (m), 1056 (w), 1008 (m), 887 (w), 808 (m), 734 (m), 653 (s,  $\text{SbF}_6^-$ ), 526 (m)  $\text{cm}^{-1}$ .

**Gold Complex 40**: At  $23^\circ\text{C}$  (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphane]gold(I) hexafluoroantimonate(V) [JohnphosAu(MeCN)SbF<sub>6</sub>, **37**]<sup>[87]</sup> (62.3 mg, 0.08 mmol, 1.8 equiv.) was added to diethyl ferrocene-1,1'-bis(2-thienyl-4-carbodithioate) (**20**, 25.0 mg, 0.04 mmol, 1.0 equiv.) in dichloromethane (5 mL). After stirring for 10 min the solvent was removed at reduced pressure, and the residue was washed with pentane (5  $\times$  5 mL). Gold complex **40** (79.5 mg, 0.04 mmol, 88%) was obtained as a dark green solid (m. p. 191–195  $^\circ\text{C}$ , dec.).

$\text{C}_{\text{Ar}}$  refers to phosphane aryl carbon atoms.  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.38 [d,  $^3J_{\text{P,H}}$  = 16.1 Hz, 36H,  $\text{C}(\text{CH}_3)_3$ ], 1.60 (t,  $^3J_{\text{H,H}}$  = 7.4 Hz, 6H,  $\text{CH}_3$ ), 3.53 (q,  $^3J_{\text{H,H}}$  = 7.4 Hz, 4H,  $\text{CH}_2$ ), 4.63–4.64 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 4.86–4.87 (m, 4H,  $\text{C}_{\text{CP}}\text{H}$ ), 7.04–7.05 (d,  $^3J_{\text{H,H}}$  = 4.4 Hz, 2H, SCCH), 7.09–7.11 (m, 4H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.22–7.24 (m, 2H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.29–7.32 (m, 4H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.36–7.39 (m, 2H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.49–7.56 (m, 4H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.83–7.87 (dt,  $^3J_{\text{H,H}}$  = 7.7 Hz, 2H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.90–7.91 (d,  $^3J_{\text{H,H}}$  = 4.4 Hz, 2H, SCCH) ppm.  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 13.2 ( $\text{CH}_3$ ), 30.8 [d,  $^2J_{\text{P,C}}$  = 6.3 Hz,  $\text{PC}(\text{CH}_3)_3$ ], 33.7 ( $\text{CH}_2$ ), 38.3 [d,  $^1J_{\text{P,C}}$  = 23.4 Hz,  $\text{PC}(\text{CH}_3)_3$ ], 70.4 ( $\text{C}_{\text{CP}}\text{H}$ ), 74.8 ( $\text{C}_{\text{CP}}\text{H}$ ), 79.5 ( $\text{C}_{\text{CP}}\text{C}$ ), 125.2 (d,  $^1J_{\text{P,C}}$  = 34.7 Hz,  $\text{PC}_{\text{Ar}}$ ), 127.5 (d,  $^2J_{\text{P,C}}$  = 6.9 Hz,  $\text{PC}_{\text{Ar}}\text{C}_{\text{Ar}}\text{H}$ ), 128.0 ( $\text{C}_{\text{Ar}}\text{H}$ ), 128.1 (SCCH), 129.0 ( $\text{C}_{\text{Ar}}\text{H}$ ), 129.8 ( $\text{C}_{\text{Ar}}\text{H}$ ), 131.4 ( $\text{C}_{\text{Ar}}\text{H}$ ), 133.5 ( $\text{C}_{\text{Ar}}\text{H}$ ), 133.7 ( $\text{C}_{\text{Ar}}\text{H}$ ), 137.0 (SCCH), 142.8 (d,  $^3J_{\text{P,C}}$  = 6.6 Hz,  $\text{PC}_{\text{Ar}}\text{C}_{\text{Ar}}\text{C}_{\text{Ar}}\text{C}_{\text{Ar}}\text{H}$ ), 143.6 ( $\text{CC}=\text{S}$ ), 149.3 (d,  $^2J_{\text{P,C}}$  = 13.2 Hz,  $\text{C}_{\text{Ar}}\text{H}$ ), 159.4 (SCC<sub>FC</sub>), 210.7 ( $\text{C}=\text{S}$ ) ppm.  $^{31}\text{P}$  NMR (162.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 63.3 ppm. IR:  $\tilde{\nu}$  = 3093 (w), 2953 (w), 2929 (w), 2870 (w), 1519 (w), 1452 (m), 1417 (m), 1323 (m), 1276 (m), 1176 (w), 1058 (m), 991 (m), 756 (m), 702 (s), 651 (s,  $\text{SbF}_6^-$ ), 526 (m)  $\text{cm}^{-1}$ .

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## Conflict of Interest

The authors declare no conflict of interest.

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