Stepwise Synthesis of Octamethylferrocene-1,1′-dicarbaldehyde. Preparation of New Electron Donors for Charge-Transfer Complexes

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A stepwise synthesis of octamethylferrocene-1,1′-dicarbaldehyde (**3**), starting from 1,2,3,4-tetramethyl-5-(methoxycarbonyl)cyclopentadiene (**7**) is described, involving ferrocene formation, ester reduction to the corresponding bis(hydroxymethyl) derivative **9**, and MnO_2 oxidation. The aldehyde **3** readily reacts with different phosphonates derived from sulfur-containing heterocycles in a Wittig−Horner reaction to form new electron donors that may be used in the preparation of various charge transfer complexes. The X-ray crystal structures of 1-[(1,3-benzodithiol-2-ylidene)methyl]-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (**11a**), 1-[(1,3-dithiolo[4,5-*b*][1,3]dithiol-2-ylidene)methyl]-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (**11b**), 1,1′-bis[(1,3-benzodithiol-2-ylidene)methyl]-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (**12a**), and 1,1′-bis[(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiol-2-ylidene)methyl]-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (**12c**) have been determined. In these compounds the planes of the sulfur heterocycles are oriented at angles of 60−75°, with respect to the plane of the respective Cp ring.

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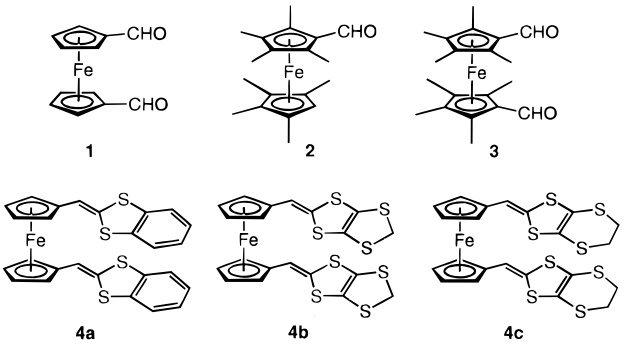
Introduction

We previously reported the use of ferrocene-1,1′-dicarbaldehyde (**1**) for the synthesis of 1,1′-disubstituted derivatives as electron donors, containing, e.g., conjugated sulfur heterocycles, and their incorporation into semiconducting and paramagnetic charge-transfer (CT) complexes.[1] Thus, compounds of type **4** (Chart 1) display preferred conformations in which the heterocycles are parallel to the respective Cp ring, thus allowing extended conjugation. As discussed previously, this structural feature is an important aspect responsible for the observed physical properties of the CT complexes. Pursuing an extension of our studies, we wanted to prepare similar derivatives in which (1) the orientation of the heterocycle is no longer parallel to the Cp and (2) the electron-donor character of the ferrocene core is increased. With these goals in mind, an obvious approach would be the introduction of alkyl substituents onto the ferrocene. Therefore, we were seeking a high-yield preparation of the corresponding octamethyl 1,1′-dicarbaldehyde (**3**). However, whereas the simple dicarbaldehyde **1** has been known for decades and is usually prepared, e.g., via the reaction of 1,1′-dilithiated ferrocene and suitable formylating reagents such as, e.g., DMF,[2] or via Vilsmeier electrophilic formylation, a comparable synthesis of the new starting material has not been reported. Steric hindrance and the strong electron-donating effect of the methyl groups appear to be the reason for the impossiblity, or at least the difficulty, of the dilithiation of octamethylferrocene with, e.g., BuLi (vide infra). Rybinskaya and co-workers adopted a completely different approach and described the oxidation of decamethylferrocene by barium manganate ($BaMnO_4$), affording a mixture of different aldehydes.[3] However, the yield of 1,1′- and 1,3-dialdehydes was in the range of ca. 10%, and the two isomers could not be separated via column chromatography. Furthermore, the reported straightforward preparation of the desired compound starting from the deprotonated form of 2,3,4,5-tetramethyl-cyclopentadienecarbaldehyde and an iron(II) salt in THF[4] could not be reproduced in our hands. We therefore developed a new convenient stepwise synthesis of aldehyde **3**, which we report herein, along with its conversion to some electron donors.

Chart 1



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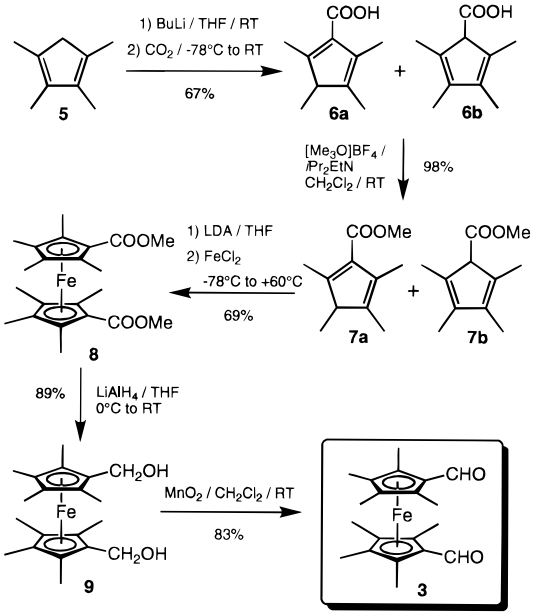
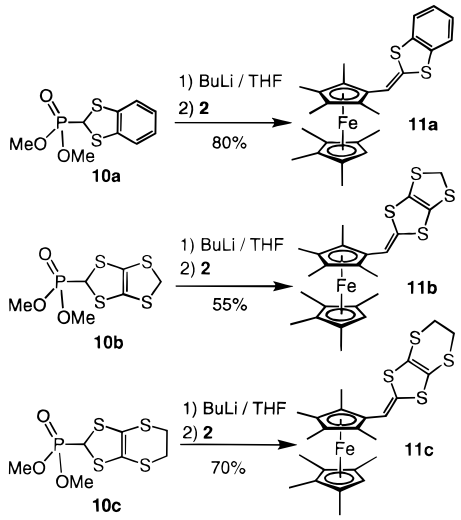
Scheme 1



Scheme 2



Results and Discussion

Synthesis of Octamethylferrocene-1,1′-dicarbaldehyde (3) and Its Derivatives. The reactions involved in the stepwise preparation of the aldehyde **3** are shown in Scheme 1.

1,2,3,4-Tetramethylcylopentadiene (**5**)[5] was subjected to lithiation during at least 12 h using *n*-, *sec*- or *tert*-BuLi. The subsequent reaction with gaseous carbon dioxide at −78 °C afforded, after workup, a mixture of the symmetric and asymmetric isomers of carboxylic acids **6** that can easily be distinguished by ^{1}H- and ^{13}C-NMR spectroscopy (see Experimental Section). The mixture of these carboxylic acids can be esterified using trimethyloxonium tetrafluoroborate. The yield of the corresponding methyl esters **7** is almost quantitative. Attempts to obtain the ester by more conventional methods, e.g., with methanol and sulfuric acid or diazomethane, were unsuccessful. Esters **7** can be deprotonated by LDA under formation of a red solution of the lithiated, air-sensitive product. The subsequent reaction with $FeCl_2$ in THF affords octamethylferrocene-1,1′-dicarboxylic acid dimethyl ester (**8**)[6,7] as a red crystalline material in a reasonable yield of about 70%. Reduction with $LiAlH_4$ or DIBAlH leads to the corresponding bis(hydroxymethyl) derivative **9**.[7] Selective oxidation of the primary alcohol groups with manganese dioxide or pyridinium chlorochromate (PCC) results in the formation of the 1,1′-dialdehyde **3** as a red crystalline product. In the former case, the yield is better (∼85%) even if the crude product needs further purification; in the latter case the yield is lower (∼40%), but the nearly analytically pure product is obtained directly from the reaction mixture without further purification.

Chart 2

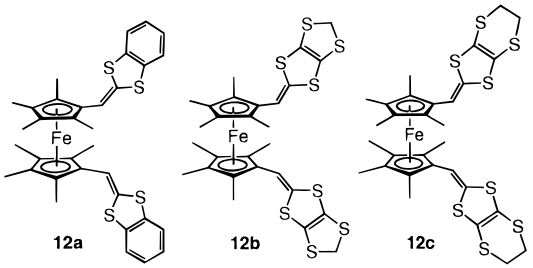


Table 1. Formal Electrode Potentials (*vs Fc/Fc*$^+$) for Ferrocene Derivatives in Dichloromethane Solution

compd	$E^{o\prime}_{0/+}$, V[a]	ΔEp, mV[a]	$E^{o\prime}_{+/2+}$, V[a]	ΔE_p mV[a]
$Fe(\eta^5\text{-}C_5Me_4H)_2$	−0.40	164		
$Fe(\eta^5\text{-}C_5Me_5)_2$	−0.48	110		
1	0.58	313		
2	−0.12	238		
3	0.15	184,[e] 164[b] 144,[e] 152[f]		
$Fe(\eta^5\text{-}C_5H_4CH_2OH)_2$	−0.01	314		
$Fe(\eta^5\text{-}C_5H_4COOCH_3)_2$	0.53	96		
4a	−0.19	86[c]	0.32	106[d]
4b	−0.20	107[c]	0.26	
4c	−0.20	84[c]	0.2	114[d]
8	−0.02	100, 94[f]		
9	−0.40	140, 148[f]		
11a	−0.40	98, 92[b]	(0.70)	
11b	−0.36	103	0.42	95
11c	−0.41	76, 90,[c] 132[d]	0.49	83
12a	−0.37	96	(0.59)	
12b	−0.33	80	(0.46)	
12c	−0.34	77	0.43	159

[a−f] Scan rates: [a]100 mV/s; [b]50 mV/s; [c]200 mV/s; [d]500mV/s; [e]25 mV/s; [f]10 mV/s. [g] All experiments carried out in dichloromethane/0.1 M (TBA)BF_4 vs 0.05 M Fc/Fc$^+$ electrode with $E^{o\prime} = +0.042$ V for ferrocene (all values are corrected for 0 V). Values in brackets are E_{pa} (anodic peak potential) only assigned to irreversible oxidation steps.

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(7) The X-ray crystal structures of **8** and **9** have been determined. The ester groups in **8** are coplanar with their respective Cp rings. The two equivalent planes containing the Fe atom, and each of the two fragments $C_{Cp}-C_{carboxylic}$ subtend an angle of 139°. **9** adopts in the solid state a conformation with local D_{5d} symmetry; i.e., the hydroxymethyl groups are oriented antiperiplanar to each other. Full experimental details of these two X-ray structural determinations, including ORTEP views of the molecules, are given as Supporting Information.

Table 2. Experimental Data for the X-ray Diffraction Study of 11a,b

	compd	
	11a	**11b**
formula	$C_{26}H_{30}FeS_2$	$C_{23}H_{28}FeS_4$
mol wt	462.5	488.5
cryst dim (mm)	0.1 × 0.2 × 0.6	0.3 × 0.3 × 0.4
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
data coll T (K)	293	293
a (Å)	7.599(9)	17.735(9)
b (Å)	8.818(10)	9.768(5)
c (Å)	17.78(2)	27.08(2)
α (deg)	95.5(1)	
β (deg)	102.08(10)	101.25(5)
γ (deg)	95.73(9)	
V (Å^3)	1151(2)	4601(4)
Z	2	8
ρ(calcd) (g·cm^{-3})	1.335	1.411
F(000)	488	2048
diffractometer	Picker-Stoe	Picker-Stoe
radiation	Mo Kα, λ = 0.710 73 Å	Cu Kα, λ = 1.541 78 Å
measd reflcns	$-8 \le h \le 7, -9 \le k \le 9, 0 \le l \le 19$	$-17 \le h \le 17, 0 \le k \le 9, 0 \le l \le 26$
2θ range (deg)	3.0−40.0	3.0−100.0
scan type	ω	ω
scan width (deg)	1.00	1.00
bkgd time (s)	0.2 × scan time	0.2 × scan time
scan speed (deg·min^{-1})	variable; 1.00−4.00 in ω	variable; 1.00−4.00 in ω
no. of indep data coll	3003	4726
no. of obsd reflcns (n_o)	2532	3542
	$\lvert F_o^2\rvert > 4.0\sigma(\lvert F\rvert^2)$	$\lvert F_o^2\rvert > 4.0\sigma(\lvert F\rvert^2)$
abs corr	N/A	face-indexed numerical
transm coeff		0.0765−0.2215
no. of params refined (n_v)	286	505
data to param ratio	8.9:1	7.0:1
quantity minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0230F^2$	$w^{-1} = \sigma^2(F) + 0.0013F^2$
R^a	0.0679	0.0389
$R_w{}^b$	0.0747	0.0568
GOF^c	0.57	1.29

^{a} $R = \sum(\lvert\lvert F_o\rvert - (1/k)\lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$. ^{b} $R_w = \sum w(\lvert\lvert F_o\rvert - (1/k)\lvert F_c\rvert\rvert)^2/[\sum w\lvert F_o\rvert^2]^{1/2}$. ^{c} GOF $= [\sum w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)^2/(n_o - n_v)]^{1/2}$.

Beside this successful preparation, some different synthetic approaches to the aldehyde **3** were attempted. A direct formylation of octamethylferrocene via the know procedure involving DMF and $POCl_3$ led to the formation of the known monoformylated product **2** only.[8] Treatment of the monoaldehyde **2** under the same conditions did not afford any bis(formylated) product. Furthermore, deprotonation of octamethylferrocene by alkyllithium reagents and subsequent reaction even with strong formylating agents such as, e.g., formyl fluoride,[9] did not afford the desired product. It appears that octamethylferrocene does not react with alkyllithium reagents at all. Treatment with an excess of BuLi at room temperature in diethyl ether over prolongued periods of time, followed by the addition of D_2O, did not give any detectable deuterium incorporation, as shown by ^{1}H- and ^{13}C-NMR spectroscopy. Finally, formylating conditions using dichloromethyl methyl ether and Lewis acids ($SnCl_4$ or $TiCl_4$)[10] led mainly to the oxidation of octamethylferrocene.

Both the monoaldehyde **2** as well as the dialdehyde **3** react with the Wittig−Horner reagents derived from phosphonates **10a**−**c**[11] affording the corresponding heterocycle-substituted octamethylferrocenes **11a**−**c** and **12a**−**c**, respectively, in moderate to good yields (Scheme 2 and Chart 2). These materials are isolated as orange microcrystals and are air-stable.

Electrochemical Properties. The electrochemical properties of the new octamethylferrocene derivatives, as measured by cyclic voltammetry, are listed in Table 1 and are compared to those of the corresponding nonmethylated compounds. The redox potentials for the first one-electron process of the simple precursors **3**, **8**, **9**, and their nonmethylated counterparts can be accounted for on the basis of approximate additive effects due to the substituents. Thus, eight methyl groups lead to a decrease of the potential by ca. 0.4 V, whereas each of the strong electron-withdrawing groups CHO and $COOCH_3$ accounts for an increase by ca. 0.25−0.30 V. On the other hand, a hydroxymethyl group exerts a negligible effect. The redox behavior of the two diester derivatives are quasi reversible in character. In both cases the peak separation is in the range of 100 mV, and the i_{pc}/i_{pa} ratio (as determined at a scan rate of 100 mV/s) is 0.81 and 0.97, respectively. The behavior

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Table 3. Experimental Data for the X-ray Diffraction Study of 12a,c

	compd	
	12a	**12c**
formula	$C_{34}H_{34}FeS_4$	$C_{30}H_{34}FeS_8$
mol wt	626.7	706.9
cryst dim (mm)	0.2 × 0.4 × 0.4	0.3 × 0.3 × 0.4
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
data coll T (K)	293	293
a (Å)	7.63(2)	10.128(4)
b (Å)	8.85(2)	12.920(4)
c (Å)	11.33(2)	12.357(5)
α (deg)	84.5(2)	
β (deg)	88.5(2)	94.52(3)
γ (deg)	82.8(2)	
V (Å^3)	756(3)	1611.9(10)
Z	1	2
ρ(calcd) (g·cm^{-3})	1.377	1.456
F(000)	328	736
diffractometer	Syntex P21	Syntex P21
radiation	Mo Kα, λ = 0.710 73 Å	Mo Kα, λ = 0.710 73 Å
measd reflcns	$0 \le h \le 7, -8 \le k \le 8, -10 \le l \le 10$	$0 \le h \le 9, 0 \le k \le 12, -11 \le l \le 11$
2θ range (deg)	3.0−40.0	3.0−40.0
scan type	ω	ω
scan width (deg)	1.00	1.00
bkgd time (s)	0.2 × scan time	0.2 × scan time
scan speed (deg·min^{-1})	variable; 2.00−6.00 in ω	variable; 2.00−6.00 in ω
no. of indep data coll	1419	1506
no. of obsd reflcns (n_o)	1092	1260
	$\lvert F_o^2\rvert > 4.0\sigma(\lvert F\rvert^2)$	$\lvert F_o^2\rvert > 4.0\sigma(\lvert F\rvert^2)$
abs corr	N/A	N/A
no. of params refined (n_v)	178	178
data to param ratio	6.1:1	7.1:1
quantity minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0050F^2$	$w^{-1} = \sigma^2(F) + 0.0019F^2$
R^a	0.0435	0.0325
$R_w{}^b$	0.056	0.0471
GOF^c	0.72	0.94

^{a} $R = \Sigma(\lvert\lvert F_o\rvert - (1/k)\lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert$. ^{b} $R_w = \Sigma w(\lvert\lvert F_o\rvert - (1/k)\lvert F_c\rvert\rvert)^2/[\Sigma w\lvert F_o\rvert^2]^{1/2}$. ^{c} GOF $= [\Sigma w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)^2/(n_o - n_v)]^{1/2}$.

of the corresponding dialcohols **9** and 1,1′-bis(hydroxymethyl)ferrocene is less reversible in character, as indicated by an i_{pc}/i_{pa} ratio of ca. 1.4 and ΔE_p values of 140 and 314 mV, respectively. We assume that under oxidative conditions water elimination may take place, under formation of a cyclic ether. The increased cathodic current can then probably be explained by a simple water reduction. The redox processes for the aldehydes **1**−**3** is only for the methylated derivatives reversible in character (i_{pc}/i_{pa} = 1.15 for the monoaldehyde **2**, 0.96 for the bis(aldehyde) **3**), whereas **1** shows a poor redox behavior (i_{pc}/i_{pa} = 0.35).

For the heterocycle-substituted ferrocenes the following trends may be identified. In the nonmethylated series **4a**−**c** the 1,1′-disubstitution accounts for a decrease of the redox potential by ca. 0.2 V. On the other hand, the influence of the sulfur heterocyclic substituents on the octamethyl derivatives **11a**−**c** and **12a**−**c** is negligible, as these compounds display first redox potentials very close to the one of octamethylferrocene, in fact even slightly higher (less negative by up to 0.06 V). This is the result of a structural difference discussed in more detail below. The presence of the methyl groups strongly disfavors a coplanar arrangement of the heterocycles with the respective Cp ring, thus impeding conjugation between these two fragments. This aspect is also reflected by the color of the compounds. Whereas derivatives **4a**−**c** are red (broad absorption maximum in the visible part of the spectrum at ca. 470 nm), the six octamethylferrocenes **11a**−**c** and **12a**−**c** are orange (maximum between 445 and 459 nm). The degree of reversibility for the first, iron-centered redox process for the donor systems **11a**−**c** and **12a**−**c** strongly depends on the scan range. Derivatives **11a**−**c** display an almost perfectly reversible redox behavior when the scanning range is limited to a maximum potential of +600 mV, relative to the appropriate $E°'$ value (i_{pc}/i_{pa} for all compounds ca. 1). A second, at least partially reversible, one-electron redox process can be observed for **11b** (i_{pc}/i_{pa} = 0.27, ΔE_p = 95 mV) and for **11c** (i_{pc}/i_{pa} = 0.4, ΔE_p = 83 mV). The corresponding 1,1′-disubstituted systems **12a**−**c** show a similar redox behavior in which a nearly reversible step (i_{pc}/i_{pa} = 0.76−1.02, ΔE_p = 77−96 mV) is followed by an irreversible or weakly reversible second step.

Solid-State Structures of 11a−b and 12a,c. In order to ascertain conformational properties of the new electron donors due to the influence of the eight methyl groups, the compounds **11a,b** and **12a,c** have been subjected to an X-ray crystallographic study. Tables 2 and 3 collect crystal and refinement parameters for **11a,b** and **12a,c**, respectively. ORTEP views of the independent molecules in the unit cells are shown in Figures 1 and 2.

The four structures turn out to be rather routine, with the bonding parameters falling in the expected ranges. Therefore, the points worth noting shall focus on common conformational properties, as these better define the overall geometry of the molecules. Thus, from this point of view, the most important feature observed for all four compounds is the orientation of the plane of the sulfur heterocycles (the least-square plane defined by

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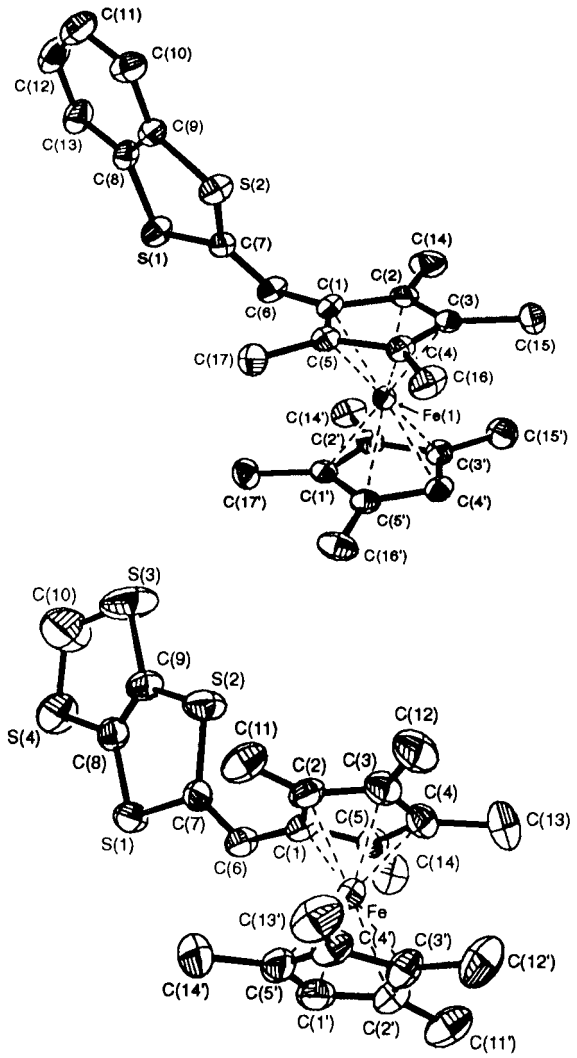

Figure 1. ORTEP views (30% probability ellipsoids) of **11a** (top) and **11b** (bottom; one of the two independent molecules per unit cell), with atom-numbering schemes. Selected bond lengths (Å) and angles (deg) are as follows. **11a**: C1−C6 1.459(6), C6−C7 1.334(6), C7−S1 1.762(5), C7−S2 1.747(6), C1−C6−C7 124.8(4), S1−C7−S2 113.7(3). **11b**: C1−C6 1.459(7), C6−C7 1.323(7), C7−S1 1.768(5), C7−S2 1.762(5), C1−C6−C7 124.8(5), S1−C7−S2 113.8(2).

the five atoms C7, S1, S2, C8, and C9 for **11a,b** and C11, S1, S2, C12, and C13 for **12a,c**, respectively) with respect to the plane of the respective Cp rings (C1−C5). For the nonmethylated parent compounds **4**, the heterocycle and the Cp ring are essentially coplanar, thus revealing extended conjugation.[1a] However, for the derivatives **11** and **12** of this study, the presence of methyl groups at the ferrocene positions adjacent to the heterocyclic substituents no longer allows such a conformation. In fact, the observed angles between the two planes defined above are as follows: 71° for **11a**, 60 and 63° for the two independent molecules in the unit cell of **11b**, 74° for **12a**, and 76° for **12c**. Such orientations interrupt the conjugation between the two π-systems in each of the molecules, thus explaining the vanishing influence of the substituents on the redox properties, as discussed above.

In compounds **11a,b** the ferrocene fragment adopts an almost perfect D_{5d} symmetric conformation, with the Cp carbon atoms bearing the heterocyclic substituent and the hydrogen, respectively, being in antiperiplanar

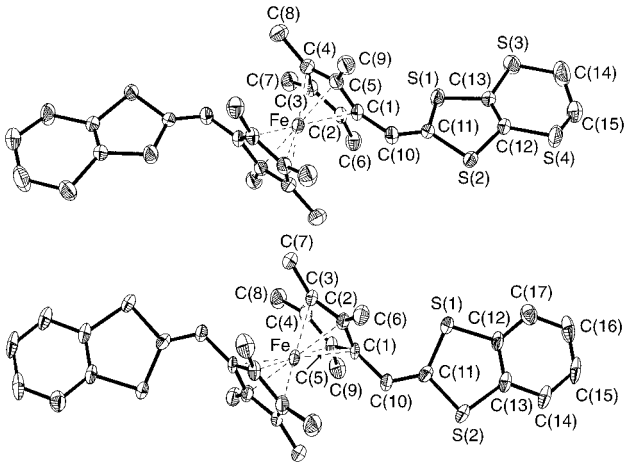

Figure 2. ORTEP views (30% probability ellipsoids) of **12a** (top) and **12c** (bottom), with atom-numbering schemes. Selected bond lengths (Å) and angles (deg) are as follows. **12a**: C1−C10 1.474(9), C10−C11 1.322(8), C11−S1 1.751(8), C11−S2 1.763(8), C1−C10−C11 123.5(5), S1−C11−S2 113.4(3). **12c**: C1−C10 1.479(6), C10−C11 1.323(6), C11−S1 1.755(4), C11−S2 1.760(4), C1−C10−C11 122.8(4), S1−C11−S2 112.5(2).

positions. For **12a,c** the antiperiplanar orientation of the substituents and hence the local D_{5d} symmetry of the ferrocene core follows from the iron atom coinciding with a crystallographic inversion center.

The planes of the sulfur heterocycles of the two independent molecules in the unit cell of **11b** (only one of which is shown in Figure 1) are roughly perpendicularly oriented to one another. Furthermore, the two fragments show relatively short intermolecular contacts, with, e.g., sulfur−sulfur distances (S1−S4′ and S4−S1′) of ca. 3.6 Å. This kind of intermolecular interaction is even more pronounced in **11a**. There, the 1,3-(benzodithiol-2-ylidene)methyl fragments are parallel, thus showing a stacking interaction, with interplanar distances of ca. 3.5 Å.

Conclusions

We have shown that octamethylferrocene-1,1′-dicarbaldehyde (**3**) is accessible by a stepwise synthesis starting from 1,2,3,4-tetramethylcyclopentadiene in an overall yield of ca. 33% (nonoptimized). Our preparation is far more reliable than previously reported ones. Compound **3** is a useful and versatile starting material for the synthesis of 1,1′-difunctional, electron-rich octamethylferrocene derivatives. The electron donors **12** are easily accessible from **3** via Wittig−Horner methods and display structural features completely different from those of their corresponding nonmethylated derivatives. We are currently pursuing the synthesis of charge-transfer complexes containing **12** and electron acceptors such as TCNQ, TCNE, $Ni(mnt)_2$, etc. and examining their solid-state physical properties. The results of these studies shall be reported in due course.

Experimental Section

General Considerations. 1,2,3,4-Tetramethylcyclopenta-1,3-diene (**5**),[5] octamethylferrocene,[12] **10a**,[11] **10b**,[11] **10c**,[11] 1,1′-

(12) (a) Koehler, F. H.; Doll, K. H. *Z. Naturforsch.* **1982**, *37b*, 144. (b) Reference 5b.

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bis(methoxycarbonyl)ferrocene,[13] 1,1′-bis(hydroxymethyl)ferrocene,[13] and ferrocene-1,1′-dicarbaldehyde[2] were prepared according to published procedures. Anhydrous $FeCl_2$ was purchased from Fluka and heated under vacuo during 3 h before use. General experimental techniques were reported earlier.[1a]

2,3,4,5-Tetramethylcyclopenta-1,4(3)-diene-1-carboxylic acid (6a) and 2,3,4,5-Tetramethylcyclopenta-2,4-diene-1-carboxylic acid (6b).[14] A 40.6 mL (56.8 mmol) amount of 1.40 M BuLi (solution in hexanes) was added to a solution of 7.074 g (57.93 mmol) of 1,2,3,4-tetramethylcyclopenta-1,3-diene (**5**) in 200 mL of THF at −20 °C. The mixture was stirred during 16 h and allowed to warm to 25 °C. The resulting thick white suspension was then cooled to −78 °C. At this temperature gaseous CO_2 was bubbled through the suspension during 15 min and the reaction mixture was allowed to warm to room temperature, while still maintaining CO_2 bubbling. After 30 min 50 mL of a saturated NH_4Cl solution and 100 mL of diethyl ether were added. The organic layer was separated and washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The remaining solid was dissolved in warm diethyl ether, and **6** (as a ca. 2:1 mixture of **6a**,**b**, by ^{1}H-NMR) was precipitated with hexanes. Yield: 6.46 g (67%) of **6a** (yellow oil) and **6b** (white solid). **6a**: ^{1}H-NMR ($CDCl_3$) δ 3.03 (m, 1H, CH), 2.28 (d, 3H, C*H*$_3$CH), 1.81 and 1.80 (2s, each 3H, CH_3), signal for COOH not detectable; ^{13}C-NMR ($CDCl_3$) δ 170.6 (COOH), 159.5, 151.3, 135.5, 131.2 (C=C), 49.6 (*C*HCH$_3$), 14.7, 14.0, 12.4, 10.6 (CH_3); MS *m/z* 166 (M^+, 100%), 151, 121, 107, 45, 28, 15. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.31; H, 8.49. **6b**: ^{1}H-NMR ($CDCl_3$) δ 3.58 (m, 1H, CH), 1.91 (s, 6H, CH_3), 1.80 (m, 6H, CH_3), signal for COOH not detectable; ^{13}C-NMR ($CDCl_3$) δ 179.9 (COOH), 139.5, 130.6 (C=C), 62.8 (*C*HCOOH), 12.2, 11.4 (CH_3).

1-(Methoxycarbonyl)-2,3,4,5-tetramethylcyclopenta-1,4(3)-diene (7a) and 1-(Methoxycarbonyl)-2,3,4,5-tetramethylcyclopenta-2,4-diene (7b).[14] A 3.50 g (21.04 mmol) amount of a mixture of the carboxylic acids **6a**,**b** was added to a suspension of 4.048 g (27.37 mmol) of trimethyloxonium tetrafluoroborate in 250 mL of dichloromethane at 0 °C. During 5 min 4.77 mL (27.37 mmol) of diisopropylethylamine was added slowly. The mixture was allowed to warm to 20 °C and stirred for 22 h. Thereafter 20 mL of 1 M HCl was added, and the organic layer was separated, washed with a saturated $NaHCO_3$ solution, and dried over $MgSO_4$. The solvent was removed in vacuo, and the remaining oil was distilled at 130−140 °C and 8 mbar. Yield: 3.519 g (98%) of a colorless oil (ca. 2:1 mixture of **7a**,**b**, as determined by ^{1}H NMR). **7a**: ^{1}H-NMR ($CDCl_3$) δ 3.74 (s, 3H, OCH_3), 3.02 (m, 1H, *H*CCH$_3$), 2.25 (d, J = 2.2 Hz, 3H, CH_3), 1.88 and 1.80 (both m, each 3H, C=CCH$_3$), 1.17 (d, J = 7.5 Hz, 3H, HCC*H*$_3$); ^{13}C-NMR ($CDCl_3$) δ 165.5 (C=O), 156.7, 149.3, 135.1, 131.7 (C=C), 50.48 (CH), 49.52 (OCH_3), 14.68, 13.72, 12.42, 10.60 (CH_3); MS *m/z* 180 (M^+), 165, 149, 133, 121 (100%), 105, 91, 77. Anal. Calcd for $C_{11}H_{16}O_2$ (mixture of **7a**,**b**): C, 73.30; H, 8.95. Found: C, 73.25; H, 8.82. **7b**: ^{1}H-NMR ($CDCl_3$) δ 3.70 (s, 3H, OCH_3), 1.80 and 1.69 (br s, each 6H, C=CCH$_3$), signal for *H*CCOO overlapping with OCH_3 signal of **7a**; ^{13}C-NMR ($CDCl_3$) δ 174.0 (C=O),145.9, 138.3 (C=C), 64.16 (CH), 51.95 (OCH_3), 12.14, 10.12 (CH_3).

1,1′-Bis(methoxycarbonyl)-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (8).[7] A solution of 10.394 g (62.5 mmol) of the methyl carboxylate **7a**,**b** in 380 mL of THF was treated with 110 mL of a freshly prepared 0.68 M LDA solution in THF (75.03 mmol) at −78 °C. The mixture was stirred during 1 h at this temperature while it turned slowly from yellow to red. After this time 6.34 g (50.02 mmol) of anhydrous $FeCl_2$ was added, together with 279 mg (5 mmol) of Fe powder (reduction of adventitious traces of $FeCl_3$).[15] The suspension was stirred and allowed to warm slowly to 20 °C during 24 h. A 200 mL volume of a saturated NH_4Cl solution was added, and the organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo, and the remaining solid was purified by flash chromatography over silica gel/ethyl acetate:hexanes (1:10). Yield: 8.928 g (69%) of a red crystalline solid. ^{1}H-NMR ($CDCl_3$): δ 3.80 (s, OCH_3), 1.96, 1.70 (both s, CH_3). ^{13}C-NMR ($CDCl_3$): δ 172.6 (C=O), 84.71, 83.74 (CpC), 67.67 (Cp *ipso*C), 10.54, 8.86 (CH_3). MS: *m/z* 414 (M^+, 100%), 383, 355, 235, 147. Anal. Calcd for $C_{22}H_{30}O_4Fe$: C, 63.78; H, 7.30. Found: C, 63.81; H, 7.41.

1,1′-Bis(hydroxymethyl)-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (9).[7] A 1.60 g (3.86 mmol) amount of the methyl ester **8** in 300 mL of THF was treated with 0.623 g (16.41 mmol) of $LiAlH_4$ at 0 °C. The suspension was stirred for 22 h while warming it slowly to 25 °C. Thereafter, 10 mL of a saturated solution of NH_4Cl and 10 mL of water were added. The mixture was extracted with diethyl ether (250 mL), dried with $MgSO_4$, and filtered over Celite. The solvent was removed in vacuo, and the remaining solid was recrystallized from acetone. Yield: 1.23 g (89%) of a yellow microcristalline solid. ^{1}H-NMR (DMSO-d_6): δ 4.24 (t, J_{HH} = 4.5 Hz, 2H, OH), 4.05 (d, J_{HH} = 4.3 Hz, 4H, CH_2), 1.65, 1.61 (both s, 24H, CH_3). ^{13}C-NMR (DMSO-d_6): δ 80.81, 79.39, 79.00 (CpC), 55.78 (CH_2), 9.51, 9.39 (CH_3). MS: *m/z* 358 (M^+), 340 (100%), 134, 119. Anal. Calcd for $C_{20}H_{30}O_2Fe$: C, 67.04; H, 8.44. Found: C, 67.03; H, 8.20.

2,2′,3,3′,4,4′,5,5′-Octamethylferrocene-1,1′-dicarbaldehyde (3). (a) With MnO_2 as Oxidant. A suspension of 2.083 g (5.814 mmol) of dialcohol **9** and 10.109 g (116.3 mmol) of manganese dioxide in 600 mL of dichloromethane was stirred during 18 h. Then, the mixture was filtered through Celite and the solvent evaporated in vacuo. The residue was purified by flash chromatography over silica gel/ethyl acetate:hexanes (1:3). Yield: 1.714 g (83%) as red crystalline solid.

(b) With Pyridinium Chlorochromate (PCC) as Oxidant. In dichloromethane, 77.6 mg (0.36 mmol) of PCC, ca. 80 mg of Celite, and ca. 80 mg of molecular sieves (4 Å) were stirred while 32.4 mg (0.09 mmol) of the alcohol **9** was added. After 3 h a solution (0.1 M) of sodium dithionite (20 mL) was added, and the organic layer was separated, washed with water, and dried over $MgSO_4$. After filtration through Celite, the solvent was evaporated in vacuo. Yield: 12.7 mg (40%) as red crystalline solid. ^{1}H-NMR ($CDCl_3$): δ 10.01 (s, 2H, CHO), 1.97, 1.75 (both s, each 12H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 196.2 (CHO), 86.82, 84.11 (cpC), 72.45 (Cp *ipso*C), 9.05, 8.71 (CH_3). MS: *m/z* 354 (M^+, 100%), 326, 297, 203, 174, 119. Anal. Calcd for $C_{20}H_{26}O_2Fe$: C, 67.81; H, 7.40. Found: C, 67.73; H, 7.41.

1-Formyl-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (2).[7] A 300 mg (1 mmol) amount of octamethylferrocene was added to a solution of 0.25 mL (2.8 mmol) of $POCl_3$ in 3 mL of DMF. The violet solution was stirred at room temperature during 1 h and then refluxed during 2 h. The mixture was then cooled to 0 °C and treated with a solution of 1.5 g of NaOAc in 10 mL of water and stirred. After 6 h the product was taken up in diethyl ether, and the organic layer was separated, washed with 1 M HCl, saturated $NaHCO_3$ solution, and brine, and dried over $MgSO_4$. After evaporation of the solvent, the

(13) For the synthesis of 1,1′-bis(methoxycarbonyl)ferrocene and 1,1′-bis(hydroxymethyl)ferrocene from ferrocene-1,1′-dicarboxylic acid see, e.g.: Gonsalves, K.; Zhan-ru, L.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3862. For the synthesis of ferrocene-1,1′-dicarboxylic acid see, e.g.: Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.

(14) The two possible asymmetric isomers **6a** and **7a** (2,3,4,5-tetramethylcyclopenta-1,4-diene-1-carboxylic acid and 2,3,4,5-tetramethylcyclopenta-1,3-diene-1-carboxylic acid and their corresponding esters) could not be distinguished by routine 1D NMR spectroscopy.

(15) The addition of iron powder to ferrous and/or ferric chloride to generate "active" $FeCl_2$ in the synthesis of ferrocenes has been previously reported. See: (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287. (b) Phillips, L.; Lacey, A. R.; Cooper, M. K. *J. Chem. Soc., Dalton Trans.* **1988**, 1383. (c) See also ref 5. For practical reasons, no experiments using the isolated THF adduct of $FeCl_2$ have been carried out. See: Aresta, M.; Nobile, C. F.; Petruzzelli, C. *Inorg. Chem.* **1977**, *16*, 1817.

product was recrystallized from diethyl ether. Yield: 225 mg (83%) of a red crystalline solid. ^{1}H-NMR ($CDCl_3$): δ 10.04 (s, 1H, CHO), 3.45 (s, 1H, CpH), 2.03, 1.83, 1.69 (all s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 195.0 (CHO), 85.8, 82.7, 81.5, 81.4 (cp), 72.4 ($C_4(Me)_4$*C*CHO), 70.9 ($C_4(Me)_4$*C*H), 11.1, 10.7, 9.5, 9.1, 8.8 (CH_3). MS: *m/z* 326 (M^+, 100%), 298, 283, 149, 121, 105, 91, 77. Anal. Calcd for $C_{19}H_{26}FeO$: C, 69.93; H, 8.05. Found: C, 69.93; H, 8.15.

1-[(1,3-Benzodithiol-2-ylidene)methyl]-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (11a). A solution of 199 mg (0.86 mmol) of phosphonate **10a** in 20 mL of THF was treated with 0.58 mL (0.88 mmol) of a 1.52 M solution of BuLi in hexanes at −78 °C. After 5 min a solution of 225 mg (0.83 mmol) of monoaldehyde **2** in 5 mL of THF was slowly added. The temperature was kept at −78 °C during 3 h. Then the mixture was allowed to warm to 20 °C and stirred during 13 h. Aqueous NH_4Cl (10 mL) and 100 mL of dichloromethane were added, after which the organic layer was separated and washed three times with a total of 150 mL of water and dried over $MgSO_4$. The solvent was evaporated in vacuo till crystallization started, and the mixture was subsequently cooled to −20 °C. Yield: 270 mg (80%) of a red crystalline solid. ^{1}H-NMR ($CDCl_3$): δ 7.13, 7.04 (m, 4H, aromatic), 6.23 (s, 1H, *H*−C=CS), 3.27 (s, 1H, $C_5(Me)_4$*H*), 1.81, 1.77, 1.73, 1.67 (all s, 24H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 136.3, 135.6, 125.0, 121.0, 120.7 (aromatic), 132.4 (C=*C*S_2), 115.5 (H*C*=CS_2), 80.7, 80.2, 80.1, 79.8, 79.1, 70.9 (Cp*C*), 10.8, 9.6, 8.9 (CH_3). MS: *m/z* 462 (M^+, 100%), 285, 231, 177, 162, 121, 105, 91. Anal. Calcd for $C_{26}H_{30}S_2Fe$: C, 67.51; H, 6.55. Found: C, 67.27; H, 6.74. UV−visible (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 446 (2.88).

1-[(1,3-Dithiolo[4,5-*b*][1,3]dithiol-2-ylidene)methyl]-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (11b). A 0.26 mL (0.42 mmol) amount of a 1.6 M *n*-BuLi solution in hexane was added over a period of 10 min at −78 °C to a solution of 101 mg (0.35 mmol) of phosphonate **10b** in 15 mL of THF. The resulting mixture was stirred for 5 min and then 114.2 mg (0.35 mmol) of the monoaldehyde **2**, dissolved in 5 mL of THF, was added dropwise over a period of 10 min. The mixture was stirred for 2 h at −78 °C and was then allowed to warm slowly to room temperature. After 18 h, 10 mL of a saturated NH_4Cl solution and 30 mL of CH_2Cl_2 were added. The organic phase was washed three times with water and dried over $MgSO_4$. The solvent was then evaporated under reduced pressure until a precipitate began to form. On cooling of the mixture to −20 °C a red-brown microcrystalline material formed. This was filtered out, dried in vacuo, and then purified by flash chromatography over silica gel/hexanes:ethyl acetate (15:1). Yield: 93.5 mg (55%) of an orange-red crystalline solid. ^{1}H-NMR (C_6D_6): δ 6.46 (s, 1H, C=CH), 3.96 (s, 2H, CH_2), 3.21 (s, 1H, C_5Me_4*H*), 1.89, 1.74, 1.73, 1.63 (all s, 24H, CH_3). ^{13}C-NMR (C_6D_6): δ 139.8 (HC=*C*S_2), 116.2, 114.9 (CS_2), 115.1 (H*C*=CS_2), 80.5, 80.3, 79.9, 79.2, 71.3 (cpC), 43.3 (CH_2), 11.07, 11.04, 11.02, 9.75, 9.69, 9.13 (CH_3). MS: *m/z* 488 (M^+, 100%), 354, 322, 244, 176, 119, 105, 91. Anal. Calcd for $C_{23}H_{28}S_4Fe$: C, 56.53; H, 5.79; Found: C, 56.63; H, 5.92. UV−visible (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 446 (2.83).

1-[(5,6-Dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiol-2-ylidene)methyl]-2,2′, 3,3′,4,4′,5,5′-octamethylferrocene (11c). An 83.5 mg (0.276 mmol) amount of phosphonate **10c** was dissolved in 50 mL of THF at −78 °C. The solution was treated with 0.17 mL (0.276 mmol) of a 1.65 M *n*-BuLi solution in hexane. After 10 min a solution of 75 mg (0.230 mmol) of monoaldehyde **2** in 20 mL of THF was added. The mixture was stirred during 1 h at −78 °C and then allowed to warm to 20 °C during another 1 h. Aqueous NH_4Cl (10 mL) and dichloromethane (50 mL) were added. The organic layer was separated, washed with water (10 mL), and dried over $MgSO_4$. The solvent was removed in vacuo and the remaining solid purified by flash chromatography over silica gel/hexanes:ethyl acetate (1:10). Yield: 81 mg (70%) of an orange solid. ^{1}H-NMR (C_6D_6): δ 6.53 (s, 1H, C=CH), 3.22 (s, 1H, C_5Me_4*H*), 2.35 (s, 4H, CH_2CH_2), 1.92, 1.75, 1.73, 1.64 (all s, 24H, CH_3). ^{13}C-NMR (C_6D_6): δ 130.4 (HC=*C*S_2), 112.7 (H*C*=CS_2), 110.8 and 109.7 (CS_2), 80.7, 80.2, 79.9, 79.5, 71.0 (cpC), 28.75 and 28.73 (CH_2CH_2), 10.81, 10.80, 9.44, 8.86 (CH_3). MS: *m/z* 502 (M^+), 474 (100%), 354, 251, 177, 119, 105, 91. Anal. Calcd for $C_{24}H_{30}S_4Fe$: C, 57.35; H, 6.02. Found: C, 57.64; H, 6.10. UV−visible (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 449 (2.85).

1,1′-Bis[(1,3-benzodithiol-2-ylidene)methyl]-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (12a). A solution of 1.883 g (7.18 mmol) of phosphonate **10a** in 300 mL of THF was treated with 4.35 mL (7.18 mmol) of a 1.65 M solution of BuLi in hexanes at −78 °C. After 5 min a solution of 1.156 g (3.263 mmol) of bis(aldehyde) **3** in 80 mL of THF was added slowly. The mixture was then allowed to warm to 20 °C and stirred during 30 min. A 20 mL volume of aqueous NH_4Cl and 150 mL of dichloromethane were added, and the organic layer was separated and washed once with 50 mL of water and dried over $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified by column chromatography with silica gel/hexane:ethyl acetate (10:1). Yield: 1.902 g (93%) of an orange crystalline solid. ^{1}H-NMR ($CDCl_3$): δ 7.16, 7.14 (m, 8H, aromatic), 6.09 (s, 2H, *H*−C=CS), 1.74, 1.70, (both s, 24H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 136.5, 135.8, 125.4, 121.0, 120.5 (aromatic), 133.2 (C=*C*S_2), 110.8 (H*C*=CS_2), 81.1, 79.6 (cp*C*), 10.5, 9.38 (CH_3). MS: *m/z* 626 (M^+, 100%), 313, 285, 133. Anal. Calcd for $C_{34}H_{34}S_4Fe$: C, 65.16; H, 5.47. Found: C, 65.43 H, 5.31. UV−visible (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 455 (2.97).

1,1′-Bis[(1,3-dithiolo-[4,5-*b*][1,3]dithiol-2-ylidene)-methyl]-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (12b). A 0.43 mL (0.65 mmol) volume of a 1.5 M *n*-BuLi solution in hexane was added over a period of 5 min to a solution of 178.0 mg (0.62 mmol) of phosphonate **10b** in 50 mL of THF at −78 °C. The resulting mixture was stirred for 5 min, and then 104.7 mg (0.295 mmol) of bis(aldehyde) **3**, dissolved in 20 mL of THF, was added dropwise over a period of 10 min. The mixture was then allowed to warm to room temperature. Aqueous NH_4Cl (10 mL) and 30 mL of CH_2Cl_2 were added. The organic phase was separated, washed with water (10 mL), and dried over $MgSO_4$. The solvent was then evaporated under reduced pressure and the resulting solid recrystallized from dichloromethane/hexane and then purified by flash chromatography over silica gel/hexanes:ethyl acetate (5:1). Yield: 54 mg (35%) of an orange-red crystalline solid. ^{1}H-NMR (C_6D_6): δ 6.36 (s, 2H, C=CH), 3.89 (s, 4H, CH_2), 1.75, 1.60 (both s, 24H, CH_3). ^{13}C-NMR (C_6D_6): δ 139.8 (HC=*C*S_2), 115.9, 114.8 (CS_2), 114.0 (H*C*=CS_2), 80.8, 80.0, 79.5 (cpC), 44.0 (CH_2), 10.5, 9.36 (CH_3). MS: *m/z* 678 (M^+), 334, 175, 136, 76 (100%). No satisfactory elemental analysis could be obtained.

1,1′-Bis[(5,6-dihydro-1,3-dithiolo-[4,5-*b*][1,4]-dithiol-2-ylidene)methyl]-2,2′,3,3′,4,4′,5,5′-octamethylferrocene (12c). A solution of 1.453 g (4.806 mmol) of phosphonate **10c** in 150 mL of THF was treated with 2.91 mL (4.806 mmol) of a 1.65 M *n*-BuLi solution in hexane at −78 °C. After 10 min a solution of 774 mg (2.185 mmol) of bis(aldehyde) **3** in 25 mL of THF was added. The mixture was then allowed to warm to 20 °C. Aqueous NH_4Cl (50 mL) and dichloromethane (150 mL) were added. The organic layer was separated, washed with water (50 mL), and dried over $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified by column chromatography with silica gel/hexane:ethyl acetate (10:1). Yield: 1.215 g (79%) of an orange solid. ^{1}H-NMR (C_6D_6): δ 6.44 (s, 2H, C=CH), 2.31 (s, 8H, CH_2CH_2), 1.80, 1.61 (both s, 24H, CH_3). ^{13}C-NMR (C_6D_6): δ 130.2 (HC=*C*S_2), 112.2 (H*C*=CS_2), 110.9 and 110.1 (CS_2), 80.8, 80.6, 79.6 (cpC), 29.77 (CH_2CH_2), 10.54, 9.33 (CH_3). MS: *m/z* 706 (M^+), 678, 650, 410, 353, 175 (100%). Anal. Calcd for $C_{30}H_{34}S_8Fe$: C, 50.97; H, 4.85. Found: C, 50.83; H, 4.93. UV−visible (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 459 (3.01).

X-ray Crystallographic Studies. Suitable crystals of compounds **8**, **9**, **11a**,**b**, and **12a**,**c** were obtained from CH_2Cl_2/hexane mixtures. Selected crystallographic and relevant data collection parameters are listed in Tables 2 and 3. Data were

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measured at variable scan speed to ensure constant statistical precision on the collected intensities. One standard reflection was measured every 120 reflections, and no significant variation was detected. The structures were solved by Patterson methods (**11a**) or direct methods (**8**, **9**, **11b**, **12a**,**c**) and refined by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms. The contribution of the hydrogen atoms in their idealized position (riding model with fixed isotropic $U = 0.080$ Å^2) was taken into account but not refined. All calculations were carried out by using the Siemens SHELXTL PLUS (VMS) system.

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Supporting Information Available: Tables of crystallographic parameters, atomic coordinates and *U* values, complete bond distances and angles, anisotropic displacement coefficients, and coordinates of hydrogen atoms for **8**, **9**, **11a**,**b**, and **12a**,**c**, and ORTEP views of **8**, **9**, and **11b**, showing both independent molecules in the unit cell (58 pages). Ordering information is given on any current masthead page. Tables of calculated and observed structure factors (47 pages) for all six compounds may be obtained from the authors upon request.

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