Charge-Transfer Salts of Ferrocene Derivatives with Bis(maleonitriledithiolato)metallate(III) Complexes ([M(mnt)₂]⁻, M=Ni, Pt): A Ground-State High-Spin [(Ni(mnt)₂)₂]²⁻ Dimer

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New hexamethylated ferrocene derivatives containing thioether moieties (1,1'-bis[(tert-butyl)thio]-2,2',3,3',4,4'-hexamethylferrocene (3a,b)) or fused S-heteropolycyclic substituents (rac-1-[(1,3-benzodithiol-2-yliden)methyl]-2,2',3,3',4,4'-hexamethylferrocene (5) and rac-1-[1,2-bis(1,3-benzodithiol-2-yliden)ethyl]-2,2',3,3',4,4'-hexamethylferrocene (14)), as well as a series of ferrocene-substituted vinylogous tetrathiafulvalenes (1,1'-bis[1,2-bis(1,3-benzodithiol-2-vliden)ethyl]ferrocene (6a), 1,1'-bis[1-(1,3-benzodithiol-2-vliden)-2-(5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-yliden)ethyl]ferrocene (6b), [1,2-bis(1,3-benzodithiol-2-yliden)ethyl]ferrocene (21a), [1-(1,3-benzodithiol-2-yliden)-2-(5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-yliden)ethyl]ferrocene (21b), [1,2-bis(5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-yliden)ethyl]ferrocene (21c), [1-(5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-yliden)-2-(1,3-benzodithiol-2-yliden)ethyl]ferrocene (21d)) were prepared and fully characterized. Their redox properties show that some of them are easily oxidized and undergo transformation to paramagnetic salts containing bis(maleonitriledithiolato)-metallate(III) anions $[M(mnt)_2]^-$ (M = Ni, Pt; bis[2,3-dimercapto- κ S)but-2-enedinitrilato(2⁻) lnickelate (1⁻) or -platinate (1⁻). The derivatives $[3a][Ni(mnt)_2]$ (26), $[3a][Pt(mnt)_2]$ (27), $[Fe\{(\eta^5-C_5Me_4S)_2S\}][Ni(Mnt)_2]$ (28), $[Fe\{(\eta^5-C_5Me_4S)_2S]][Ni(Mnt)_2]$ (28), $[Fe\{(\eta^5-C_5Me_4S)_2S]][Ni(Nnt)_2]$ (28), $[Fe\{(\eta^5-C_5Me_4S)_2S]]$ $C_{Me_4}(3)_{S}[Pt(mnt)_2]$ (29), [5] $[Ni(mnt)_2] \cdot ClCH_2CH_2CI$ (30), [6a] $[Ni(mnt)_2]$ (31), [6a] $[Ni(mnt)_2] \cdot ClCH_2CH_2CI$ (30), [6a] $[Ni(mnt)_2]$ (31), [6a] $[Ni(mnt)_2] \cdot ClCH_2CI$ (30), [6a] $[Ni(mnt)_2]$ (31), [6a] $[Ni(mnt)_2] \cdot ClCH_2CI$ (30), [6a] $[Ni(mnt)_2]$ (31), [6a] $[Ni(mnt)_2] \cdot ClCH_2CI$ (30), [6a] $[Ni(mnt)_2] \cdot CLCH_2CI$ (ClCH₂CH₂Cl (**31a**), [**6a**] [Pt(mnt)₂] [**32**), and [**6b**] [Ni(mnt)₂] (**33**) were prepared and fully characterized, including by SQUID (superconducting quantum interference device) susceptibility measurements. X-Ray crystal-structural studies of the neutral ferrocene derivatives 6a,b, 21c,d, and 1,1'-bis[1-(1,3-benzodithiol-2yliden)-2-oxoethyl]ferrocene (23), as well as of the charge-transfer salts 26-28, 30, and 31a, are reported. The salts 28 and 30 display both a D⁺A⁻A⁻D⁺ structural motif, however, with a different relative arrangement of the $[{Ni(mnt)_2}_2]^{2-}$ dimers, thus giving rise to different but strong antiferromagnetic couplings. Salt 26 exhibits isolated ferromagnetically coupled $[{Ni(mnt)}_{2}]^{2-}$ dimers. Salt 27 displays a D⁺A⁻D⁺A⁻ structural motif in all three space dimensions, and a week ferromagnetic ordering at low temperature. Salt **31a**, on the contrary, shows segregated stacks of cations and anions. The cations are connected with each other in two dimensions, and the anions are separated by a 1,2-dichloroethane molecule.

1. Introduction. – We recently reported synthesis and characterization of bis(maleonitriledithiolato)metallate(III) salts $[M(mnt)_2]^-$ (M=Ni, Co, Pt; bis[2,3-di(mercapto- κS)-but-2-enedinitrilato(2-)]metallate(2-)) with the octamethylferrocenyl thioethers [1] **1** and **2**, as well as with ferrocenes containing S-heterocycles [2-3] related to the basic tetrathiafulvalene (TTF) structure. These compounds were shown to display weak ferromagnetic or antiferromagnetic interactions. The physical properties of such materials strongly depend on the relative arrangement of cations and anions in the solid state. In turn, the three-dimensional structure is influenced by the nature and size of the S-containing substituents on the ferrocene. In continuation of these investigations concerning charge-transfer (CT) complexes with ferrocene electron

donors [1-7], a series of bis(maleonitriledithiolato)nickelate and -platinate complexes with a variety of new ferrocenes (see 3-6) were prepared. The aim of the present study was to further explore how subtle changes at the electron-donor molecular level influence the material properties of the corresponding CT complexes. Thus, the present work was conducted on two main lines. First, in the ferrocenyl thioether series, the new hexamethyl derivatives **3** and **4** were prepared, thus allowing a comparison with their octamethyl counterparts. Can such a minor structural change significantly alter the properties of the corresponding CT complexes? Second, a more drastic modification of the benzodithiol-containing derivatives, *i.e.*, towards branched compounds comprising up to four heterocyclic units (see **6**), could lead to multiple intermolecular interactions in the solid state.



2. Results and Discussion. – 2.1. Synthesis of Ferrocene Derivatives as Electron Donors. 2.1.1. Hexamethylated Ferrocenes. As opposed to tetramethylcyclo-penta-1,3-diene, 1,2,3-trimethylcyclopenta-1,3-diene (10) is not stable and dimerizes slowly at room temperature and upon distillation. Because the *retro-Diels-Alder* reaction of dimeric 10 does not occur as easily as for dicyclopentadiene, this compound is more difficult to access [8][9]. However, 10 may be obtained by distillation of trimethylcyclopent-2-en-1-ols (9) at atmospheric pressure and at 170° and has to be used directly, after removal of the co-distilled water with sodium sulfate. Thus, for the synthesis of 1,1'-bis[(*tert*-butyl)thio]-2,2',3,3',4,4'-hexamethylferrocene (3), a strategy for the direct conversion of trimethylcyclopentenone 7 to the S-substituted ligand 8 was needed. As

illustrated in *Scheme 1*, **8** was obtained in moderate yields applying a reported method [10][11]. The synthesis of the corresponding ferrocenes **3** was then achieved analogously to that of the octamethylated counterparts [1]. The product obtained was a 1:1 mixture of two diastereoisomers, *i.e.*, an achiral *meso*-form **3a** and a pair of enantiomers **3b** that could be distinguished by NMR spectroscopy. In particular, the cyclopenta-2,4-dien-1-yl (Cp) protons of **3a** and **3b** show distinctly different chemical shifts in the ¹H-NMR spectrum. Upon recrystallization from hexane, an enriched sample (diastereoisomer ratio of 85:15) was obtained. However, the configurational assignment of the diastereoisomers could be made only *via* an X-ray crystallographic study of the corresponding CT [Ni(mnt)₂] salt (*vide infra*) obtained from the enriched mixture. This revealed that the enriched component is the *meso*-form **3a**, thus making a complete assignment of the [Ni(mnt)₂] salt with sodium dithionite afforded the ferrocene **3a** quantitatively, and contaminated with only 6% of **3b**.



The 1,1',2,2',3,3'-hexamethylferrocene (11) was needed as a starting material for the preparation of the corresponding mono- and dialdehydes, intermediates in the synthesis of donor molecules containing fused S-heterocycles such as, e.g., 5 [2-4][6][12]. As opposed to what was observed for the octamethylated derivatives previously reported from our laboratory [4][6], it was anticipated that the Sheterocycles in the hexamethylated series would assume an orientation coplanar with the Cp ring and, therefore, be in conjugation with the ferrocene. Hexamethylferrocene 11 was obtained in moderate yield from crude 10 as shown in *Scheme 2*. The dilithiation of 11, but not of the corresponding octamethyl derivative, with butyllithium (BuLi) in the presence of N.N.N'.N'-tetramethylethylenediamine (TMEDA) appears to be possible. However, the followup products upon reaction with DMF and sulfur, respectively, *i.e.*, the dialdehyde **15** and the trithioferrocene **16**, could be isolated in yields of a few percent only. Even the use of stronger bases such as *tert*-butyllithium or 'Lickor' [13] did not improve these preparations. Further work with 15 and 16 was, therefore, discontinued. On the other hand, monosubstitution of 11 could be achieved more easily. Thus, the monoaldehyde 12 was prepared via a Vilsmeier reaction, as in the case of the octamethylated derivative [14-16]. The following Wittig-Horner reaction afforded the new ferrocene donor 5 in good yield. In an attempt to further formylate 5 under *Vilsmeier* conditions, we found a selective functionalization of the olefinic C-H bond, and not at the second Cp ring. This reaction opens the possibility to

prepare a new class of donor molecules belonging to the class of vinylogous tetrathiafulvalenes [17-26]. Indeed, aldehyde **13** reacted in an additional *Wittig-Horner* reaction to give the new donor **14**. Finally, one should note that compounds **5** and **12**– **14** are chiral and that they were obtained as racemates.



2.1.2. Ferrocenes Containing Vinylogous Tetrathiafulvalenes. The formylation reaction described above prompted us to prepare a series of vinylogous TTF compounds based on non-methylated ferrocene, for which the accessibility of monoand 1,1'-disubstituted derivatives was known [2]. Thus, the monosubstituted ferrocenes **19a** and **19b** were prepared in very good yields from **17** and **18a** or **18b**, respectively (*Scheme 3*). As expected, these compounds could be selectively converted under *Vilsmeier* conditions to the aldehydes **20a** and **20b**, respectively, in high yields. However, aldehyde **20b** required the reagent oxalyl chloride instead of phosphoric

trichloride, which gave no detectable product. From the intermediates 20a,b, the four vinylogous ferrocenyl tetrathiafulvalenes 21a - d were prepared in moderate to good yields by *Wittig-Horner* reactions.



Finally, from the known precursor 22a, the ferrocene derivatives 6a and 6b containing two vinylogous tetrathiafulvalenes were obtained in good yields *via* 23 (*Scheme 4*). In contrast, 22b did not react under the same conditions as 22a, neither with oxalyl chloride nor with phosphoric trichloride. It appears that ferrocene oxidation of 22b prevails under these conditions, as indicated by the green color of the reaction mixture.

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2.1.3. Synthesis of Charge-Transfer Complexes 26-33. The preparation of $[M(mnt)_2]^-$ salts 26-33 (M=Ni, Pt) containing the donors 3-6 was achieved according to the published procedure by reaction with the ferrocenium bis(maleoni-triledithiolato)metallates 24 or 25 (see Scheme 5) [1][3]. With the new ferrocenebridged, vinylogous bis(tetrathiafulvalene) **6a** and $[Ni(mnt)_2]^-$ salt **24**, two different products **31** and **31a** were obtained in ratios close to 1:1 from dichloroethane solutions. One of them, **31a**, is the dichloroethane adduct which crystallized in nice prismatic plates, whereas the second one, **31**, is the solvent-free 1:1 salt, obtained as extremly thin needles. The $[Pt(mnt)_2]^-$ salt **32** of **6a** and the $[Ni(mnt)_2]^-$ salt **33** of **6b** could be isolated in only moderate yields. All new $[M(mnt)_2]^-$ salts described in this study

display sharp $\tilde{\nu}(CN)$ bands in the narrow range between 2205 and 2209 cm⁻¹. This is also true for the starting monoanionic forms $(Et_4N)[M(mnt]_2]$. The IR opacity of the dichloroethane adduct **31a** down to 3000 cm⁻¹ is indicative of a semiconductor-like behavior of this compound.



2.2. Cyclovoltammetric Measurements. Routine cyclovoltammetric measurements in CH_2Cl_2 solution were carried out for all new ferrocene compounds, to check their ability to form CT complexes. Redox potentials are reported in *Table 1*. The ferrocenes **3a,b, 5, 6a,b, 11, 12, 15**, and **16** all show one reversible one-electron oxidation. The redox potential increases by *ca*. 0.3 V per aldehyde group, and *ca*. 0.1 V per thioether group, as compared to the corresponding non-substituted derivatives.

The two donors **5** and **14** show two reversible oxidation waves. The lower one concerns the ferrocene unit, whereas the second process corresponds to an oxidation of the S-substituent. Cyclovoltammograms for the three compounds **5**, **13**, and **14** are depicted in *Fig. 1*. The two one-electron processes in **5** are separated by 0.78 V (*Table 1*). In **14**, the oxidation of the ferrocene occurs at a slightly higher potential than in **5**. This can be explained by the larger steric hindrance of the substituent on **14**, such that a coplanar geometry with the Cp ring is no longer possible, thus reducing the delocalization of the positive charge on the substituent. The second oxidation step, which is a reversible two-electron oxidation, is lowered by 0.14 V, as compared to **5**. Thus the two potentials are separated by only 0.61 V. The aldehyde group of **13** increases the redox potential of the ferrocene by 0.13 V. This is much less than the effect of an aldehyde group directly attached to the Cp ring. Moreover, **13** shows a second irreversible oxidation at a potential of +1.09 V.

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Compound (reduced form)	$E^{\circ\prime}{}_{(0 ightarrow n+)} \left[\mathbf{V} ight]$	$\Delta E_{\rm p} [{\rm mV}]$	$i_{ m pc}/i_{ m pa}$	$E^{\circ\prime}{}_{(n+\rightarrow m+)}$ [V]	$\Delta E_{p} [mV]$	$i_{ m pc}/i_{ m pa}$
3a,b	$(-0.19^{b})_{(0\to 1)}$	104	0.95			
4	$(-0.10^{\circ})_{(0\rightarrow 1)}$	272	1.00			
5	$(-0.35^{\circ})_{(0\rightarrow 1)}$	132	0.96	$+0.43^{\circ})_{(1\rightarrow2)}$	140	1.13
ба	$-0.16^{\circ})_{(0\to 1)}$	106	1.05	$\begin{array}{l} (+0.24)^{\rm b})_{(1-2)} \\ (+0.33)^{\rm b})_{(2-3)} \\ (+0.70)^{\rm b})_{(3\rightarrow4)} \\ (+0.80)^{\rm b}_{(4\rightarrow5)} \\ (+0.37)^{\rm b})_{(5\rightarrow3)} \text{VIIb}^{\rm e}) \end{array}$		
6b	$-0.16^{d})_{(0-1)}$	98	1.8	$\begin{array}{l} (+ \ 0.04)^{\rm b})_{(3 \rightarrow 1)} {\rm VIIa^{\rm e}}) \\ (+ \ 0.14)^{\rm e})_{(3 \rightarrow 1)} \\ (+ \ 0.13)^{\rm d})_{(1 \rightarrow 2)} \\ (+ \ 0.21)^{\rm d})_{(2 \rightarrow 3)} \\ + \ 0.57^{\rm d})_{(3 \rightarrow 4)} {\rm VIa^{\rm e}}) \\ (- \ 0.03)^{\rm d})_{(3 \rightarrow 1)} {\rm VIb^{\rm e}}) \\ (+ \ 0.05)^{\rm b})_{(3 \rightarrow 1)} \end{array}$	224	
11	$(-0.34^{b})_{(0\rightarrow 1)}$	404	0.96			
12	$(-0.03^{\circ})_{(0\rightarrow 1)}$	120	0.97			
13	$(-0.22^{\circ})_{(0\to 1)}$	205	1.39	$(+1.09)^{b})_{(1\rightarrow 2)}$		
14	$(-0.32^{\circ})_{(0\to 1)}$	136	1.02	$+0.29^{\circ})_{(1\rightarrow2)}$	164	0.97
15	$+0.23^{b})_{(0\to 1)}$	92	0.94			
16	$(-0.03^{\circ})_{(0\rightarrow 1)}$	112	0.98			
19a	$(-0.07^{b})_{(0\rightarrow 1)}$	110	0.69	$+0.455^{b})_{(1\rightarrow2)}$	119	0.31
19b	$(-0.08^{\circ})_{(0-1)}$	96	0.88	$+0.30^{\circ})_{(1-2)}$	192	1.6
20a	$+0.04^{\circ})_{(0,1)}$	58	0.97	$(+0.78)^{b}_{(1-2)}$		
20b	$+0.03^{b})_{(0,1)}$	200	0.81	$(+0.84)^{b}$		
21a	-0.08^{b}	98	0.96	$+0.20^{b}$ (1.2)	86	
)(0→1)			$+0.36^{b})(2-2)$	166	
21h	-0.07^{b}) (a. 4)	107		$+0.13^{b}$ (2-3)	56	
-10	$(0.07)_{(0\to 1)}$	107		$+ 0.13^{b})_{(1 \rightarrow 2)}$	118	
210	0.10%)	00		$+ 0.04^{\circ})_{(2 \rightarrow 3)}$	00	
210	$(0.10)_{(0\to 1)}$	20		$(0.00)_{(1\to 2)}$	130	
01 J	0.100)	127		$+ 0.34)_{(2 \rightarrow 3)}$	130	
210	$-0.10^{-})_{(0\to 1)}$	13/		$+0.14^{-})_{(1\rightarrow 2)}$	138	
23	$+0.02^{b})_{(0\to 1)}$	102	0.97	$(+0.55^{-})_{(2\rightarrow3)}$ $(+0.78)^{b}_{(1\rightarrow2)}$	108	

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

^a) All experiments were carried out in dry CH₂Cl₂/0.1M (Bu₄N)BF₄ vs. 0.05M Fc/Fc⁺ reference electrode with $E^{\circ\prime} = +0.042$ V for ferrocene, and a Pt working electrode (all values are corrected for 0 V). Values in brackets are E_{pa} or E_{pc} (anodic or cathodic peak potentials), assigned only to irreversible oxidation steps. ΔE_{p} is the difference between E_{pa} and E_{pc} and i_{pc}/i_{pa} is the ratio between cathodic and anodic current indicative of the reversibility of the redox process. ^b) Scan rate 100 mV/s. ^c) Scan rate 20 mV/s. ^d) Scan rate 50 mV/s). ^e) See *Fig. 3* for peak identification.

The two mono-substituted ferrocenes **19a** and **19b** can both be oxidized twice. The first one-electron oxidation again is probably located on the ferrocene moiety, whereas the second corresponds to an electron removal from the substituent [2][6]. The potential of the first oxidation is ca. 100 mV higher than in the doubly substituted analogues. The two oxidation steps are not completely reversible, as shown by the ratio of the anodic and cathodic currents of 0.31 and 1.6, respectively (*Table 1*).



Fig. 1. Cyclovoltammograms of the three ferrocene donors 5, 13, and 14

Both aldehydes **20a** and **20b** can be reversibly oxidized at a potential of +0.04 and +0.03 V, respectively (*Table 1*). Here again, the potentials increase by *ca*. 110 mV with respect to that of the precursors because of the acceptor group. At a potential of +0.78 and +0.84 V, respectively, a second irreversible oxidation occurs similarly to what is observed for the aldehydes **13** and **23**. The latter can be reversibly oxidized at a potential of +0.02 V, and an irreversible oxidation occurs at +0.78 V (see below, *Fig. 3*).

The four vinylogous tetrathiafulvalenes 21a - d show three oxidation waves (*Fig. 2*). Because the three waves are overlapping, the ratios of the anodic and cathodic currents could not be determined. However, since the cycles overall are closed, probably no

decomposition of the compounds occurs. In all four cases, the reduction wave at the highest potential is very steep, and the corresponding current is higher than expected for a normal one-electron reduction step. Such effects can be detected when a conducting species precipitates at the electrode. Such behavior has been reported, for example, for $[Ni(dmit)_2]$ derivatives [27] (dmit^{2–} = 1,3-dithiol-2-thione-4,5-dithiolato = 4,5-di(mercapto- κS)-1,3-dithiol-2-thione).



Fig. 2. Cyclovoltammograms of the four vinylogous TTF derivatives 21a-d

Donor **6a** displays an interesting redox behavior (see *Fig. 3*), as it is possible to oxidize this compound in five descrete one-electron steps (steps I-V). However, the waves corresponding to the oxidations from **6a**¹⁺ to **6a**³⁺ (steps II and III) and from **6a**³⁺

	6a	6b	21c	21d	23
Empirical formula	$C_{42}H_{26}FeS_8$	$C_{40}H_{30}Cl_4FeS_{12}$	$C_{22}H_{18}FeS_8$	C24H28FeS6	$C_{28}H_{18}FeO_2S_4$
$M_{\rm r}$	843.00	1093.01	594.76	554.62	570.51
Crystal size/mm	$0.57 \times 0.27 \times 0.19$	$0.3\times0.3\times0.06$	$0.1 \times 0.02 \times 0.02$	$0.2\times0.1\times0.1$	$0.7\times0.3\times0.3$
Crystal system	triclinic	triclinic	orthorhombic	orthorhombic	monoclinic
Space group (No.)	P1 (2)	$P\bar{1}(2)$	$P2_{1}2_{1}2_{1}$ (19)	$P2_{1}2_{1}2_{1}$ (19)	$P2_1/c$ (14)
Temp.	room temp.	room temp.	room temp.	room temp.	room temp.
a/Å	14.170(3)	10.327(5)	11.799(10)	11.7920(3)	12.804(5)
b/Å	14.364(3)	13.002(7)	12.869(7)	12.9689(4)	14.716(6)
c/Å	20.603(4)	17.059(9)	15.478(12)	15.1203(4)	13.443(6)
a/deg	99.33(3)	90.70(2)	90	90	90
β/deg	106.27(3)	98.84(2)	90	90	111.42(3)
γ/deg	109.52(3)	98.43(2)	90	90	90
$V/Å^3$	3639.5(13)	2238(2)	2350(3)	2312.34(11)	2358(2)
Ζ	4	2	4	4	4
ρ (calc.)/g cm ⁻³	1.538	1.622	1.681	1.593	1.607
μ/mm^{-1}	0.906	10.388	1.363	1.206	1.021
Diffractometer	Stoe image	Picker Stoe	Syntex P21	Siemens Smart	Syntex P21
	plate diffraction			Platform with	
	system			CCD detector	
Wavelength $\lambda/\text{\AA}$	MoK_a ,	CuK_a ,	MoK_a ,	MoK_a ,	MoK_a ,
0	$\lambda = 0.71073$	$\lambda = 1.54178$	$\lambda = 0.71073$	$\lambda = 0.71073$	$\lambda = 0.71073$
θ Range/deg	3.96-24.71	1.31 - 25.00	2.06 - 20.03	2.07-32.89	2.14 - 20.04
Measured reflections	21561	4601	1281	7850	2203
Observed reflections $(n)^a$	10865	4601	1281	7850	2203
Parameters refined (n)	919	523	281	255	316
Abs_correction	none	integration	integration	empirical	integration
u max/min trans	none	0 581/0 111	0.652/0.590	(SADABS)	0 774/0 717
WR_{a} $(I > 2\sigma(I)^{b})$	0 1139	0.1515	0.0513	0.0656	0.0620
$R_{1}(I > 2\sigma(I)^{c})$	0.0480	0.0530	0.0198	0.0341	0.0232
Gof on F^{2d}	1 022	1 046	1.012	0.889	1.062
Res electron density	0.564	0.731	0.160	0.234	0.164
eÅ ⁻³	0.007	0.751	0.100	0.237	0.107

Table 2. Experimental Data for the X-Ray Diffraction Studies of 6a,b, 21c,d, 23, 26-28, 30, and 31a

to $6a^{5+}$ (steps IV and V) strongly overlap. Furthermore, the reduction part of the cycle shows only three waves, where two two-electron reductions (steps VI and VIIb) and one one-electron reduction (step VIIIb) can be detected. A two-electron reduction wave is observed also deriving from cation $6a^{3+}$ (VIIa), however at a peak potential higher by *ca*. 100 mV, as compared to the potential of the corresponding step (VIIb) observed in the full cycle. As in the case of the monosubstituted analogues 21a - d, the closed redox cycles indicate that no compound degradation is occurring.

2.3. Solid-State Structure of Neutral Donor Molecules and Charge-Transfer Salts. 2.3.1. Preamble. Single-crystal X-ray diffraction studies were carried out for the five neutral ferrocene derivatives 23, 6a,b, and 21c,d, and the five CT salts 26-28, 30, and 31a. Table 2 gives the relevant crystal and data-collection parameters. Bond distances and angles of each asymmetric unit were found to fall in the expected ranges and shall, therefore, not be discussed in detail. It was mainly of interest to see how the geometry and orientation of the substituents on the ferrocenes-moiety change in going from the

	26	27	28	30	31a
Empirical formula	C32H28FeN4NiS6	C ₃₂ H ₃₈ FeN ₄ PtS ₆	C ₂₆ H ₂₄ FeN ₄ NiS ₇	C ₃₄ H ₃₀ Cl ₂ FeN ₄ NiS ₆	C ₅₂ H ₃₀ Cl ₂ FeN ₄ NiS ₁₂
M _r	785.59	921.96	731.48	872.44	1281.02
Crystal dimens/mm	$0.3 \times 0.24 \times 0.16$	$0.2\times0.2\times0.2$	$0.4 \times 0.3 \times 0.25$	$0.4 \times 0.25 \times 0.04$	$0.6 \times 0.4 \times 0.2$
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
Space group (No.)	$P2_1/n$ (14)	Pbca (61)	$P2_1/c$ (14)	<i>P</i> 1 (2)	C2/c (15)
Temp.	room temp.	room temp.	room temp.	room temp.	room temp.
a/Å	12.48290(10)	13.297(39)	9.804(5)	9.537(5)	8.309(4)
b/Å	16.9929(3)	16.849(5)	11.392(8)	11.120(6)	23.202(12)
c/Å	18.54960(19)	17.301(9)	27.96(2)	18.691(9)	27.982(14)
a/deg	90	90	90	83.39(4)	90
β /deg	102.4630(10)	90	93.89(6)	77.83(3)	94.52
γ/deg	90	90	90	75.46(49)	90
$V/\text{\AA}^3$	3842.03	3876(3)	3116	1872(2)	5378
Ζ	4	4	4	2	4
ho(calc.)/g cm ⁻³	1.358	1.580	1.559	1.548	1.582
μ/mm^{-1}	1.220	4.329	1.563	8.424	8.202
Diffractometer	Siemens Smart	Syntex P21	Syntex P21	Picker Stoe	Picker Stoe
	Platform with				
	CCD detector				
Wavelength λ/Å	MoK_a ,	MoK_a ,	MoK_a ,	CuK_a ,	CuK_a ,
	$\lambda = 0.71073$	$\lambda = 0.71073$	$\lambda = 0.71073$	$\lambda = 1.54178$	$\lambda = 1.54178$
θ Range/deg	1.64 - 21.98	2.28 - 20.04	1.93-17.53	1.21 - 25.00	1.59 - 25.00
Measured reflections	4685	1819	2164	3845	2772
Observed reflections	4685	1819	1990	3845	2772
Parameters refined	399	209	371	433	327
(p)					
Abs. correction	empirical	none	empirical	integration	integration
μ , max/min trans.	(SADABS)		$(\psi \text{ scan})$	0.712/0.173	0.207/0.061
$wR_2 (I > 2\sigma(I)^b)$	0.0954	0.0480	0.0676	0.1436	0.1346
$R_1 (I > 2\sigma(I)^c)$	0.0433	0.0221	0.0315	0.0554	0.0507
G.o.f. on $F^{\wedge} 2^d$)	1.043	0.689	0.889	1.049	1.130
Res. electron density eÅ ⁻³	0.366	0.509	0.407	0.856	0.435
^{a)} $(F_o^2 > 4.0\sigma(F ^2))$ $[\sigma (w(F_o^2 - F_c^2)^2]/(n-p)]$	b. b) $wR_2 = [\sigma(p_1)]^{1/2}$.	$w(F_{\rm o}^2 - F_{\rm c}^2)^2]/\sigma[w$	$(F_{\rm o}^2)^2]^{1/2}$. c) F	$R_1 = \sigma F_o - F_c /\sigma F_o$. d) G.o.f. = $S =$

Table 2. (cont.)

neutral to the oxidized form, and how the arrangement of these groups influences the ordering of the anions.

2.3.2. *Neutral Donor Molecules.* First, it is important to note that the vinylogous TTF fragment seems to be very flexible, such that weak packing forces have a strong influence on its conformation. Thus, in all measured structures, except for the isomorphous **21c** and **21d**, the relative arrangement of this fragment is different, although ¹H-NMR spectra in solution indicate free rotation of these substituents.

The dialdehyde **23** crystallizes in the monoclinic space group $P2_1/c$, and a view of the molecule is shown in *Fig. 4*. The two Cp rings are almost parallel (interplanar angle 2.5°), eclipsed, and rotated by only 3.9° against each other. Thus, the two substituents lie one above the other; however, they are not coplanar with the respective Cp plane, but rotated by 36 and 30°, and the two benzodithiol fragments *R* and *R'* are not parallel,



Fig. 3. Cyclovoltammograms of the two ferrocene-bridged vinylogous TTF derivatives 6a and 6b and of their precursor 23

with an interplanar angle 14.4° . The distances between the planes of the two neighboring benzene rings are between 3.88 and 4.52 Å, which is larger than a *van der Waals* stacking distance. The two aldehyde groups lie in the same plane as the benzodithiol fragments, as indicated by the distances of the O-atoms from the corresponding planes of 0.3 Å for O(1) and 0.02 Å for O(1'). There are quite short contacts between the S- and O-atoms of 2.66 and 2.61 Å, respectively. Also, the bond distances C(6)-C(14) and C(6')-(14') are shorter than expected (1.440(4) and 1.436(5) Å, resp.). Both anomalies may indicate a contribution of a thienium/enolate resonance structure, thus with an attractive S-O interaction.

Crystals of the ferrocene-bridged vinylogous TTF derivative **6a** are triclinic (space group $P\overline{1}$) with two different molecules per asymmetric unit. These two molecules,



Fig. 4. ORTEP Plot of dialdehyde 23 with the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level; H-atoms are omitted.

indicated hereafter as M_A and M_B , with the benzodithiol fragments R1 and R1' (closer to the Cp ring), and R2 and R2' (further away from the Cp ring), respectively, are enantiomers (*Fig. 5*). The molecules are pseudo- C_2 -symmetric with eclipsed and parallel Cp rings that are rotated against each other by 79 (M_A) and 68° (M_B). The benzene rings in the fragments R1 and R1' stack in a 'face-to-face' geometry with distances of 3.64 (M_A) and 3.89 Å (M_B), slightly larger than van der Waals contacts. The corresponding interplanar angles are 2.7 (M_A) and 2.9° (M_B). On the other hand, the fragments R2 and R2' are almost perpendicular to the fragments R1 and R1', with torsion angles C(7)-C(6)-C(14)-C(15) of 83 and 79° (M_A), and -94° and -86° (M_B), thus indicating that there is no conjugation between R1 and R2.

The very similar ferrocene-bridged TTF derivative **6b** also crystallizes in the triclinic space group $P\overline{1}$. However, crystals contain two CH₂Cl₂ molecules per asymmetric unit, one of which is highly disordered (see *Fig. 6*). Again, the two Cp rings are eclipsed (interplanar angle 5.8°) and rotated against each other by 86°. The two fragments RI/RI' and R2/R2' are again not coplanar. The torsion angle C(8)-C(6)-C(7)-(15) is -68° (and -141° for the corresponding angle of RI' and R2'). With respect to **6a**, the most striking difference is that the two benzene rings of the fragments R1 and R1' in **6b** show an 'edge-to-face' interaction with an interplanar angle of 60° and a distance of the two ring centers of 5.1 Å.

The vinylogous ferrocenyl-substituted TTF derivatives **21c** and **21d** are isomorphous and crystallize in the non-centrosymmetric space group $P_{2_12_12_1}$. A view of the asymmetric unit of **21c** and **21d**, along with the atom-numbering scheme, is depicted in *Fig.* 7. Like the compounds **6a** and **6b**, the vinylogous TTF substituents are not planar, and the fragment *R1* is not coplanar to the respective Cp ring. The interplanar angle between *R1* and *R2* is 58° for **21c** and 56° for **21d**. The torsion angle C(7)-C(6)-C(12)-C(13) is $64^{\circ}(-67^{\circ})$, and the plane of *R1* forms an angle with the Cp ring of 42° (48°).

2.3.3. *Charge-Transfer Complexes.* The apparently small difference between [*meso*-Fe{ η^5 -C₅Me₃(S'Bu)}₂][Ni(mnt)₂] (**26**) and the corresponding octamethylated derivative [1] has a remarkably strong influence on the relative arrangement of the molecules in the solid state. Thus, whereas the latter displays a typical D⁺A⁻D⁺A⁻ structure, in **26**



Fig. 5. ORTEP Plot of the asymmetric unit with the two enantiomers M_A and M_B in **6a**, with the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level; H-atoms are omitted.



Fig. 6. ORTEP Plot of the asymmetric unit of the ferrocene bridged vinylogous TTF derivative **6b**, with the atomnumbering scheme. Thermal ellipsoids are drawn at the 30% probability level; for clarity reasons, the second position of the C-atom C2M in the disordered solvent molecule (occupancy 25%), as well as H-atoms, are omitted.

there are layers of ferrocenium cations alternating with layers of $[(Ni(mnt)_2)_2]^{2-}$ anion pairs, running diagonally through the unit cell. A projection along the *b* axis of a pair of such layers is depicted in *Fig. 8*, and a projection along the *a* axis is given in *Fig. 9*. It is apparent that the anion dimers are well separated from each other. Within each dimer, the two anions are arranged in such a way that each Ni-atom lies above the C=C bond of the neighboring unit (see also below, *Fig. 17*). A consequence of this arrangement is that two pairs of S-atoms lie above each other with intermolecular S–S distances of 3.72 Å, and that the Ni–Ni distance becomes quite large (4.54 Å). Another feature of this structure is that the $[Ni(mnt)_2]^-$ units quite strongly deviate from planarity, as indicated by the interplanar angle between the two mnt ligands of 10.4° . To the best of our knowledge, this type of structure in $[Ni(mnt)_2]^-$ dimers has never been observed before and, as we will see, has an important effect on the magnetic properties of the CT complex **26**. Finally, the cations show a pseudo-centrosymmetric conformation, with parallel Cp rings (interplanar angle $< 0.5^\circ$) rotated against each other by 178° .

The platinum derivative **27** crystallizes in the orthorhombic space group *Pbca*, with both the Fe- and the Pt-atoms on symmetry centers. Thus, every cation is completely surrounded by six anions, resulting in a three-dimensional $D^-A^+D^-A^+$ motif. A projection of a layer perpendicular to the *c* axis is depicted in *Fig. 10*. Within such a layer, four $[Pt(mnt)_2]^-$ anions assume a propeller-like arrangement around the cation (symmetry center), with an interplanar angle of 74° within each pair. One of the nitrile groups points almost directly to the Pt-atom of the neighboring anion, with a Pt-N distance of 5.77 Å. The same N-atom has an equal distance to the Fe-center. The three different Fe-Pt distances are 6.65 Å along *a*, 8.42 Å along *b*, and 8.65 Å along *c*, corresponding to half-cell constants. The Cp ring of the cation is almost parallel to the anions in the *a* direction (interplanar angle 7.2°).



Fig. 7. ORTEP Plot of the asymmetric unit of the vinylogous TTF derivatives **21c** and **21d** with the atomnumbering scheme. Thermal ellipsoids are drawn at the 30% probability level; H-atoms are omitted.



Fig. 8. Perspective view of a ferrocenium and [Ni(mnt)₂]-layer of 26 projected along the b axis

The CT complex **28** of the 1,1',2,2,',3,3,',4,4'-octamethyl-5,5'-trithioferrocene (**4**) and $[Ni(mnt)_2]^-$ crystallizes in the monoclinic space group $P2_1/c$ and displays a D+D+A-A-D+D+A-A- motif. The structure consists of alternating planes of almost perpendicular stacks. A projection along one of the stacking directions is depicted in *Fig. 11*, and a side view of a stack is detailed in *Fig. 12*. Two anions from two neighboring layers form an interplanar angle of 74°. The $[Ni(mnt)_2]^-$ dimers have structural features as previously found in other compounds [1][28][29], with each Ni-atom interacting with a S-atom of the companion fragment at a distance of 3.78 Å.



Fig. 9. Perspective view of a ferrocenium and [Ni(mnt)2]-layer of 26 projected along the a axis

Furthermore, the Ni-atoms show a weak interaction with the terminal S-atom of the trithio unit at a distance of 3.86 Å. The Cp ring of the cation is almost perfectly parallel to the anion plane, with an interplanar angle of less than 2° . The cations within a pair are facing each other with an intermolecular distance between the middle disordered S-atoms of 3.53 Å, similar to what was found for the corresponding [FeCl₄]⁻ and (TCNQF₄)⁻ salts [5][7] ((TCNQF₄)⁻ = '2,3,5,6-tetrafluorotetracyanoquinodimethanide').

A comparable description may be applied to the structure of the triclinic **30**, crystallizes in the space group $P\bar{1}$. Again a D⁺D⁺A⁻A⁻D⁺D⁺A⁻A⁻ motif is observed, however, with the anions being almost congruent one above the other, with Ni–Ni (3.64 Å) and S–S (3.56 Å and 3.65 Å) interactions, as shown in *Fig. 13*. As opposed to the octamethylated derivatives previously reported by *Hobi et al.* [4][6], the S-heterocycle in the cation resulting from **5** is almost coplanar to the Cp ring, with an

1342



Fig. 10. Perspective view of a layer of cations and anions perpendicular to the c axis in 27

interplanar angle between the Cp ring and the heterocycle of 11°. A cation/anion interaction exists, as represented by a Ni–S contact distance of 3.80 Å of one of the two S-atoms. The other one has short-range interactions (3.66 and 3.59 Å) with two S-atoms of a $[Ni(mnt)_2]^-$ dimer in the neighboring layer. Two neighboring donor molecules constitute an enantiomeric pair, with a symmetry center located between the two parallel benzene rings. The planes of the latter are separated from each other by *ca*. 3.66 Å, slightly larger than typical *van der Waals* contacts. Finally, there is one dichloroethane molecules form a zig-zag arrangement parallel to the *b* axis, with alternating short (3.35 Å) and long (3.45 Å) Cl–Cl-distances.

Compound **31a** crystallizes in the monoclinic space group C2/c with segregated stacks of donor and acceptor molecules. The acceptor stacks contain intercalated dichloroethane molecules, thus leading to a large Ni–Ni distance of 8.31 Å. The ferrocene molecules adopt a chiral conformation and lie on the twofold axes parallel to the *b* axis. All molecules aligned on one such C_2 axis show the same orientation and absolute configuration. Thus, enantiomerically pure stacks of each enantiomer alternate along the *c* axis, as evident from both the projection of the unit cell along the *a* axis in *Fig.* 14 and a projection along the C_2 axis in *Fig.* 15. The overall conformation of the ferrocenium cations is very different from that of the neutral



Fig. 11. Perspective view of the unit cell of 28, projected along one stacking direction

molecule **6a**. The two Cp rings show an eclipsed conformation with the two substituents directly above each other, and a relatively large opening of 13° in the direction of the substituents. Thus, the distances C(3)-C(4') and C(4)-C(3') are shortened to 3.17 Å and C(1)-C(1') is elongated to 3.69 Å from the value of 3.37 Å in ferrocene. The orientation of the two heterocyclic fragments *R1* is such that only the five-membered



Fig. 12. Side view of a $A^-A^-D^+D^+A^-A^-$ stack in 28

rings overlap to a significant extent, with relatively short distances of 3.75 Å between S(2) and S(2'). The two fragments *RI* and *R2* are now more planar than in the neutral molecule. The torsion angle around the bond C(6)-C(14) within the vinylogous TTF unit is 147° (83°, 94° in neutral **6a**). Thus, this unit approaches coplanarity of the two heterocycles (interplanar angle of 34°) much more than does the neutral molecule, where the two fragments are almost perpendicular to each other. A significant conjugation and hence delocalization of positive charge is therefore possible, despite the rotation by 47° of the substituents with respect to the Cp ring. Donor-donor intermolecular interactions are also apparent. Along the *a* axis, *e.g.*, the atoms S(1) in fragments *RI* are separated by 3.57 Å, which is significantly shorter than *van der Waals* distance (3.7–4.1 Å). Moreover, along the *c* axis, the fragments *R2* show a plane-toplane distance of 3.5 Å, which corresponds to the *van der Waals* distance of the S- and



Fig. 13. Perspective view of a layer of **30**, projected perpendicular to the layer plane. Contacts which are shorter than van der Waals distances are indicated by dotted lines. The dichloroethane molecules fill the empty space between two $D^+A^-A^-D^+$ packages.

C-atoms. This leads to a two-dimensional network of stacking interactions between donor molecules (*Fig. 14*). The perfectly planar anions, which lie on a symmetry center, fill the space between the layers of the ferrocenes and are, therefore, strongly separated. The shortest contact of a S-atom of the anion and R2, *e.g.*, is more than 4 Å.

2.4. Magnetic Measurements. Magnetic-susceptibility measurements were carried out for the CT complexes 26-31a with a SQUID (superconducting quantum interference device) susceptometer in the temperature range between 2 and 300 K at a constant external field of 1000 Gauss. All compounds except **31a** obey a modified *Curie-Weiss* expression (*Eqn. 1*), where q is the sum of core diamagnetism and temperature-independent paramagnetism (TIP)¹). For all compounds, q is positive, meaning that TIP is larger than the diamagnetic component.

$$\chi_{\rm mol} = \frac{C}{T - \theta} + q \tag{1}$$

¹) $q = \text{sum of } \chi_{\text{DIA}} \text{ and } \chi_{\text{TIP}}; \langle g_A \rangle = 2.01 \text{ [37]}.$



Fig. 14. *Perspective view of the unit cell of* **31a**, *projected along the a axis*. Numbering of the atoms and fragments as described in the text.



Fig. 15. Perspective view of a ferrocenium layer of **31a**, projected along the b axis. There are short contacts between the S-atoms S(1) (3.57 Å, dotted lines) of the fragments *R1*.

A plot of $\chi_{mol}T$ vs. T for the six compounds is shown in Fig. 16. The magnetic properties of the CT complexes are strongly influenced by the relative arrangement of the molecular components in the crystal. In principle, there are two main structural classes, *i.e.*, one with separated single anions and cations assuming a D⁺A⁻D⁺A⁻ arrangement, and showing ferromagnetic interactions (*e.g.* **27**) [1][30], and a second group containing dimers of anions, this being the more common case. This second group can in turn be divided in two subgroups: those with isolated dimers displaying a D⁺A⁻A⁻D⁺ motif (for example **28** and **30**), and those with segregated stacks of anion dimers and columns of cations. For this second category, many examples have been reported [1][3][28][30-32]. Weiher and co-workers [31] found in 1964 that the tetraethylammonium salts of [{M(mnt)₂}₂]^{2⁻} (M = Ni, Pt) have a singlet ground state (S=0) with a thermally populated excited triplet state (S=1). These authors used the

equation developed by *Figgis* and *Martin* [33] $(Eqn. 2)^2$) to calculate the molar magnetic susceptibility of dimeric $[{M(mnt)_2}_2]^{2-}$ complexes, and found an energy gap between singlet and triplet state J_{AA} ($S=0 \rightarrow S=1$) for $(Et_4N)[Ni(mnt)_2]$ of 620 cm⁻¹.

$$\chi_{\rm mol} = \frac{N\beta^2 \langle g_{\rm A} \rangle^2 S_{\rm A} (S_{\rm A} + 1)}{kT(3 + e^{-J_{\rm AA}/kT})} + \chi_{\rm DIA} + \chi_{\rm TIP}$$
(2)

Twenty years later, Ramakrishna [34] showed that this is not a sufficiently accurate description because, in a stack of anions with alternating distances, alternating J values should be observed. It has been shown that these values are extremely sensitive to the packing arrangement of the dimers. Unfortunately, it is not easy to discern the two different values from only temperature-dependent susceptibility measurements, because there are too many parameters to fit. However, Eqn. 2 can be used as long as the observed J values are interpreted as average values for all possible interactions. A survey of the magnetic data of the new compounds, together with some selected literature data, are given in Table 3.



Fig. 16. SQUID Susceptibility data for compounds 26–30 and 31a measured in an external field of 1000 G. The lines correspond to the calculated values either with Eqn. 1 (26, 27) or Eqn. 4 (28–30, 31a).

With the assumption that there are no interactions between the ferrocenium donors and the $[{Ni(mnt)_2}_2]^{2-}$ dimers, the magnetic susceptibility of both components is additive (*Eqn. 3*) [35]. This assumption is meaningful whenever the metal-metal distances between donors and acceptors are sufficiently large. For both contributions, χ_{donor} and $\chi_{acceptor}$, a term as in *Eqn. 2* can be used to calculate the molar magnetic susceptibility of the compounds containing $[{M(mnt)_2}_2]^{2-}$ dimers, as given by *Eqn. 4*.

²⁾ N, Avogadro constant; β, Bohr magneton; (g_A), average Landé factor of the acceptors; S_A, spin of the acceptors; k, Boltzmann constant; J_{AA}, energy difference between ground and excited state; χ_{DIA}, diamagnetic susceptibility; χ_{TIP}, temperature-independent paramagnetic susceptibility.

	<i>Curie</i> constant <i>C</i> [cm ³ Kmol ⁻¹]	μ_{eff} [$\mu_{\mathrm{b}}\mathrm{mol}^{-1}$]	Weiss Const. θ [K]	$J_{ m AA}$ [cm ⁻¹]	$J_{ m DD}$ [cm ⁻¹]	$\langle g_{ m D} angle$	$q \cdot 10^{-6}$ [cm ³ mol ⁻¹]
26	0.917(5)	2.71	+1.3(2)	_	_	2.40	1031(17)
27	0.554(4)	2.10	+3.0(49)	-	-	1.37	631(18)
28	0.559(5)	2.11	+0.7(3)	-302(8)	-0.27(5)	2.588(5)	607(25)
29	0.6048(4)	2.20	-0.197(4)	< -1000	-0.459(9)	2.9035(9)	1047(3)
30	0.402(6)	1.79	+1.3(6)	-630(33)	-1.01(7)	2.192(8)	477(36)
31a	0.451(5)	1.90	-6.0(59)	-96(1)	-2.34(3)	2.280(3)	1889(4)
$(Et_4N)[Ni(mnt)_2][29][31]$	-		-	- 620	_	2.06[37]	- 260
$(Ph_{3}MeP)[Ni(mnt)_{2}][28][31]$	-		-	-490	-	2.06[37]	-150
$(Et_4N)[Pt(mnt)_2][31][32]$	-		-	- 350	-	2.04[37]	-220
$[1][Ni(mnt)_2][1][7]$	0.88(2)	2.65	-0.7(9)	-6(1)	+0.6(4)	2.65(4)	720(50)
$[Fe(\eta^5-C_5H_4CHCHPhSMe)_2]-[Ni(mnt)_2] [3][6]$	0.480(4)	1.96	+0.7(4)	- 771(4)	-0.81(3)	2.692(4)	626(15)

 Table 3. Survey of the Observed Magnetic Data for the Charge-Transfer Complexes 26-30 and 31a, as well as for Some Selected Previously Reported Compounds

$$\chi_{\rm mol} = \chi_{\rm donor} + \chi_{\rm acceptor} + \chi_{\rm DIA} + \chi_{\rm TIP} \tag{3}$$

$$\chi_{\rm mol} = \frac{N\beta^2}{kT} \frac{\langle g_{\rm D} \rangle^2 S_{\rm D}(S_{\rm D}+1)}{3 + e^{-J_{\rm DD}/KT}} + \frac{\langle g_{\rm A} \rangle^2 S_{\rm A}(S_{\rm A}+1)}{3 + e^{-J_{\rm AA}/KT}}$$
(4)

We shall address the CT complexes 28 and 30 first, as they contain isolated $[Ni(mnt)_2]^-$ dimers displaying a known arrangement within the D+A-A-D+ motif. Furthermore, although the crystal structure of 29 is not known, the magnetic data strongly indicate that its structure must be very similar to that of 28. Thus, for these compounds, the *Curie* constants C are too small for one unpaired electron per donor and acceptor molecule (C = 0.559(5) cm³K/mol and $\mu_{eff} = 2.11 \ \mu_B \text{mol}^{-1}$ for 28³); C =0.6048(4) cm³K/mol $\mu_{\rm eff} = 2.20 \,\mu_B {\rm mol}^{-1}$ for **29**; $C = 0.402(6) {\rm cm}^3 {\rm K/mol}$ and $\mu_{\rm eff} =$ $1.79 \,\mu_{\rm B}$ mol⁻¹ for **30**). By fitting the observed data with Eqn. 4, strong antiferromagnetic interactions for all three compounds result, as expected (28: $J_{AA} = -302(8)$ cm⁻¹ and $J_{\rm DD} = -0.27(5) \text{ cm}^{-1}$; **29**: $J_{\rm AA} < -1000 \text{ cm}^{-1}$ and $J_{\rm DD} = -0.459(9) \text{ cm}^{-1}$; **30**: $J_{\rm AA} = -0.459(9) \text{ cm}^{-1}$; (33) cm⁻¹ and $J_{\rm DD} = -1.01(7)$ cm⁻¹). The higher value of $J_{\rm AA}$ for **30**, as compared to 28, can be explained by the relatively strong direct Ni-Ni interaction, whereas in 28, a Ni-S-Ni interaction is found. In the Pt derivative 29, the coupling constant J_{AA} is too large for it to be obtained by means of magnetic-susceptibility measurements. In other words, in the measured temperature range below 300 K, only the contribution of the cation is observed. Because of the relatively short distances of one S-atom of the donors to the Ni-atom of the acceptors in 28 and 30, a D^+A^- interaction could be expected. However, below 100 K, the triplet state of the $[{Ni(mnt)_2}]^-$ dimers is no longer thermally populated, such that the contribution of an interaction between donor and acceptor has no significant influence on the magnetic susceptibility below this temperature.

The magnetic behavior of **31a** is more complex, as it does not obey the *Curie-Weiss* expression (*Eqn. 1*). Nevertheless, a *Curie* constant *C* of 0.451(5) cm³K/mol ($\mu_{eff} = 1.90 \,\mu_{B} \text{mol}^{-1}$) and a negative *Weiss* constant θ of -6.0(5) K could be determined. The

³) As obtained from high-temperature data according to $\mu_{\rm eff} = (3k\chi_{\rm mol} \cdot T/N\beta^2)^{1/2})$, calculated per 1 mol of Fe.

 $\chi T vs. T$ plot (*Fig. 16*) shows a steady decrease with a small plateau at about 25 K and a strong drop below 10 K. This behavior points out strong antiferromagnetic interactions. Although it is possible to obtain perfect coincidence between values calculated with *Eqn. 4* and the observed measured data, the resulting values for J_{AA} and J_{DD} probably do not have any physical meaning. It is indeed known from the crystal structure (*vide supra*) that there are several contacts between the donor molecules and also between donors and acceptors, possibly leading to magnetic couplings.

As opposed to the above compounds, **26** shows a strong increase in χT as a function of T below 20 K (Fig. 16). The Curie constant C of 0.917(5) cm³K/mol (μ_{eff} = 2.71 $\mu_{\rm B}$ mol⁻¹) indicates that there has to be an unpaired electron per donor and acceptor molecule ($S = 2 \times 1/2$ spin system). Thus, the hitherto unknown arrangement of the $[Ni(mnt)_2]^-$ anions within a dimer changes the sign of the spin-spin interaction. This is the first time that an isolated $[{Ni(mnt)_2}_2]^{2-}$ dimer with a ferromagnetic (S = 1) ground state has been found. A comparable situation was reported for the [Ni(dmit)] salt of decamethylferrocenium [36]. This observation can now help to explain the unusually weak antiferromagnetic interaction in the previously described compound [1] [Ni(mnt)₂] [1]. In this compound, stacks of $[{Ni(mnt)_2}_2]^2$ dimers are found, like in (Et_4N) [Ni(mnt)₂]. However, the interdimer interaction is probably a ferromagnetic one as in 26, of almost the same magnitude as the antiferromagnetic intradimer interaction. Such an alternation of ferromagnetic and antiferromagnetic interactions leads to the overall weak antiferromagnetic J_{AA} value of only -6(1) cm⁻¹. A summary of the observed magnetic properties of [Ni(mnt)2]- dimers in different CT complexes, along with a view of the different dimer arrangements, is depicted in Fig. 17.

Compound 27 shows behavior similar to that of its companion 26, with the difference that the *Curie* constant *C* is too small for it to indicate the presence of one unpaired electron per molecular unit $(C = 0.554(4) \text{ cm}^3\text{K/mol}, \mu_{\text{eff}} = 2.10 \,\mu_B \text{mol}^{-1})$. This can be explained only with an exceptionally small average *Landé* factor $\langle g_D \rangle$ for the ferrocenium cation of only 1.37 ($\langle g_A \rangle$ for [Pt(mnt)₂]⁻ = 2.04 [37]). Below 20 K, again a strong increase is observed in the $\chi T vs. T$ plot (*Fig. 16*), indicating a weak but significant ferromagnetic ordering at low temperature, as shown also by the positive *Weiss* constant θ of +3.04(4) K. This observation is in accord with the D⁺A⁻D⁺A⁻ arrangement of the molecules found in the solid state.

3. Conclusions.- We have shown that it is possible to achieve ferromagnetic interactions in molecular materials containing $[M(mnt)_2]^-$ anions by two completely different interaction pathways. One of them is the already known mechanism relying upon a D⁺A⁻D⁺A⁻ structural motif, as in compound **27**. The second one is based on the new dimer arrangement found in $[meso-Fe{\eta^5-C_5HMe_3(S'Bu)}_2][Ni(mnt)_2]$ (**26**), leading to a dimer with a ferromagnetic ground state. Therefore, it should be possible, in principle, to obtain a one dimensional stack of ferromagnetically coupled $[M(mnt)_2]^-$ anions, as long as the cation would favor such a relative arrangement of the anions. However, we have seen how serendipitous and unpredictable the structural properties of $[M(mnt)_2]^-$ CT complexes are, also in view of the structural variety of the ferrocenyl donor molecules. Thus, the goal remains to find ferromagnetic compounds with higher T_c 's than for the D⁺A⁻D⁺A⁻ complexes of decamethyl ferrocene with TCNE (tetracyanoethylene = ethenetetracarbonitrile) and TCNQ (= tetracyano-

[Fe{(η⁵-C₅Me₄S)₂S}][Ni(mnt)₂] 28



 $[Fe{\eta^5-C_5HMe_3{(bdt)CH_2}}(\eta^5-C_5H_2Me_3)][Ni(mnt)_2](C_2H_4Cl_2) 30$



 $[meso-Fe{\eta^5-C_5HMe_3(S'Bu)}_2][Ni(mnt)_2]$ 26



 $[Fe{\eta^5-C_5Me_4(SMe)}_2][Ni(mnt)_2]$



Fig. 17. Different arrangements of $[[Ni(mnt)_2]_2]^{2-}$ dimers, with their magnetic interaction parameters J. In the ferromagnetically coupled compound **26**, the value of J could not be determined, because of an overparameterization.

quinodimethane = 2,2'-(cyclohexa-2,5-diene-1,4-diylidene) bis[propanedinitrile]) reported by *Miller* and others [38–41]. We are currently performing quantum-mechanical calculations aimed at finding the relative energy differences in the three different dimer arrangements, and to calculate the triplet/singlet energy gap in **26**.

Experimental Part

General. Experimental techniques were described earlier [2]. NMR: at 250.13 (¹H) and 62.895 MHz (¹³C) for CDCl₃ solns. at 25°, unless stated otherwise; δ in ppm rel. to SiMe₄ (= 0 ppm), *J* in Hz. MS: *m/z* (rel. %). *1-[*(tert-*Butyl*)*thio*]-2,3,4-trimethylcyclopenta-1,3-diene (**8**). A soln. of 2,3,4-trimethylcyclopent-2-en-1-one [8][9][42-46] (**7**; 4.958 g, 39.9 mmol) in THF (100 ml) was mixed with titanium tetrachloride (6.77 g,

35.7 mmol) at 0°, and sodium 1,1-dimethylethanethiolate (4.475 g, 39.9 mmol) and Et₃N (5.56 mL, 39.9 mmol) were added dropwise. The mixture was warmed to r.t. and stirred overnight. The solvent was evaporated and the residue distilled at $110^{\circ}/3 \cdot 10^{-2}$ mbar in a bulb-to-bulb distillation apparatus: 4.56 g (58%) of **8**. Bad smelling yellow oil. ¹H-NMR: 1.28 (*s*, *t*-Bu); 1.83 (*s*, 1 Me); 1.94 (*s*, 1 Me); 2.01 (*s*, 1 Me); 3.02 (*m*, CH₂). ¹³C-NMR: 11.30 (Me); 13.39 (Me); 13.56 (Me); 31.44 (*Me*₃C); 46.95 (Me₃C); 52.16 (CH₂); 124.83 (MeC); 136.40 (MeC); 138.85 (MeC); 142.65 ('BuSC). EI-MS: 196.3 (42; *M*⁺⁺), 140 (100), 125, 107.

1,1'-Bis[(tert-butyl)thio]-2,2',3,3',4,4'-hexamethylferrocene (mixture of diastereoisomers 3a/3b). The same procedure as for 1,1'-bis[(*tert-butyl*)thio]-2,2',3,3',4,4',5,5'-octamethylferrocene [1] was applied, with 8 (4.15 g, 21.1 mmol), THF (30 ml), a freshly prepared lithium diisopropylamide (LDA) soln. (from ($^{i}Pr)_2NH$ (4.5 ml), 1.6M BuLi in hexane (17 ml), and THF (25 ml)), and anh. iron(II) chloride (2.08 g, 29.6 mmol): 2.89 g (70%) of **3a/3b** 1:1. M.p. 101°. By recrystallization from hexane, the *meso*-form **3a** could be enriched to a *meso/rac* ratio of 85:15 after one recrystallization.

Data of **3a**: ¹H-NMR: 1.15 (*s*, 2 *t*-Bu); 1.79 (Me); 1.84 (Me); 1.86 (Me); 3.67 (*s*, 2 CH (Cp)). ¹³C-NMR: 10.32 (Me); 10.99 (Me); 11.75 (Me); 30.84 (*Me*₃C); 44.89 (Me₃C); 74.94 (CH (Cp)); 78.07 (BuSC); 83.11 (MeC (Cp)); 83.48 (MeC (Cp)); 86.05 (MeC (Cp)).

Data of **3b**: ¹H-NMR: 1.15 (*s*, 2 *t*-Bu); 1.80 (*s*, 2 Me); 1.81 (*s*, 2 Me); 1.85 (*s*, 2 Me); 3.78 (*s*, 2 CH (Cp)). ¹³C-NMR (62.895 MHz, CDCl₃): 10.09 (Me); 10.49 (Me); 11.90 (Me); 30.82 (*Me*₃C); 44.94 (Me₃C); 74.78 (CH (Cp)); 77.62 (^BuSC); 83.31 (MeC (Cp)); 83.40 (MeC (Cp)); 86.04 (MeC (Cp)).

Data of **3a/3b**: IR (KBr): 3072, 2957, 2897, 1655, 1472, 1456, 1377, 1360, 1290, 1169, 1032, 977, 836, 750, 696, 518, 457. EI-MS: 446 (100, M^{++}), 390, 334, 301, 299, 193, 162, 105. Anal. calc. for C₂₄H₃₈FeS₂ (893.1): C 64.55, H 8.58, S 14.36; found: C 64.68, H 8.51, S 14.41.

Synthesis of **3a** by Reduction of the Corrresponding $[Ni(mnt)_2]^-$ Salt **26**. [**3a** $][Ni(mnt)_2]$ (**26**; 754 mg) was vigorously stirred in sodium dithionite soln.//BuOMe until the black crystals dissolved. The red aq. soln. containing $[Ni(mnt)_2]^2^-$ was separated and the org. phase dried (MgSO₄) and evaporated: 425 mg (99%) of **3a**. M.p. 134–136°. ¹H-NMR: *meso/rac* 94:6.

2,3,4-Trimethylcyclopent-2-en-1-ol (9) [47]. To a soln. of 7 (10 g, 80 mmol) in Et₂O (100 ml), LiAlH₄ (3.4 g, 90 mmol) was added in portions. The resulting mixture was stirred for 24 h at r.t. Then, 2N HCl was slowly added until the excess of LiAlH₄ was hydrolyzed. The org. phase was filtered over *Celite*, and the lithium and aluminium salts were washed with 'BuOMe. The combined org. phase was evaporated and the residue distilled at 94°/4 mbar in a bulb-to-bulb distillation apparatus. 8.74 g (87%) of 9 *cis/trans ca.* 3:1. GC/EI-MS: 126 (20, M^{+*}), 111, 43, 29, 15 (100).

1,1',2,2',3,3'-Hexamethylferrocene (**11**). At 1 atm/170° (bath) **9** (7.5 g, 59 mmol) was distilled. At this temp., trimethylcyclopentadiene distilled together with H₂O (boiling temp. 92°) directly into a cooled *Schlenk* tube (-78°), to prevent *Diels-Alder* dimerization. When the distillation was complete, pentane was added to the distillate and the soln. dried (MgSO₄) and evaporated at 0°.5 g (47.8 mmol, 81%) of 1,2,3-trimethylcyclopenta-1,3-diene (**10**). This product was immediately cooled to -78°, mixed with THF (10 ml) and 2M LDA in THF/ ethylbenzene (31 ml, 62 mmol), and stirred for 15 min. Anh. iron(II) chloride (4.6 g, 36 mmol) was added in one portion and the mixture allowed to warm to r.t. The resulting mixture was dissolved in 'BuOMe and treated with 2N HCl and brine. The residue from the org. phase was chromatographed (silica gel, hexane): 2.4 g (30%) of **11**. IR (KBr): 3068, 2902, 1475, 1377, 1030, 802, 474. ¹H-NMR: 1.79 (*s*, 2 Me); 1.85 (*s*, 4 Me); 3.61 (*s*, 4 CH (Cp)). ¹³C-NMR: 9.66 (Me); 12.19 (Me); 68.44 (CH (Cp)); 80.82 (MeC); 82.01 (MeC). EI-MS: 270 (100, M^{++}), 255, 160, 148, 135, 105, 91. Anal. calc. for C₁₆H₂₂Fe (270.2): C 71.12, H 8.21; found: C 71.10, H 8.14.

rac-*1-Formyl-2,2',3,3',4,4'-hexamethylferrocene* (**12**). A mixture of **11** (2.4 g, 8.8 mmol), DMF (14 ml), and POCl₃ (2.4 ml, 26.4 mmol) was stirred overnight. A sat. NaOAc soln. was added and the resulting mixture stirred for an additional hour. The product was extracted with CH₂Cl₂ and chromatographed (silica gel, hexane/AcOEt 3:1): 1.65 g (63%) of **12**. M.p. 128°. IR (KBr): 3065, 2965, 2907, 1666, 1412, 1380, 1157, 1033, 844, 799, 744, 721, 684, 656, 612, 510, 470. ¹H-NMR: 1.69 (*s*, Me); 1.76 (*s*, Me); 1.77 (*s*, Me); 1.88 (*s*, Me); 1.94 (*s*, Me); 2.09 (*s*, Me); 3.65 (*d*, 1 CH (Cp)); 3.69 (*d*, 1 CH (Cp)); 4.25 (*s*, 1 CH (Cp)); 9.89 (*s*, CHO). ¹³C-NMR: 194.54 (CHO): 87.89 (MeC (Cp)); 87.35 (MeC (Cp)); 84.39 (MeC (Cp)); 83.98 (MeC (Cp)); 83.29 (MeC (Cp)); 82.43 (MeC (Cp)); 75.02 (MeC (Cp)); 70.24 (CH (Cp)); 69.98 (CH (Cp)); 69.82 (CH (Cp)); 12.25 (Me); 11.73 (Me); 11.59 (Me); 10.25 (Me); 9.66 (Me); 9.17 (Me). EI-MS: 298 (100, M^+), 269, 255, 240, 163, 148, 107, 91, 79, 56. Anal. calc. for C₁₇H₂₂FeO (298.2): C 68.47, H 7.44; found: C 68.33, H 7.42.

rac-1-[(1,3-Benzodithiol-2-ylidene)methyl]-2,2',3,3',4,4'-hexamethylferrocene (5). A soln. of dimethyl 1,3benzodithiol-2-ylphosphonate [48–50] (**18a**; 106 mg, 0.404 mmol) in THF (15 ml) was mixed with 1M BuLi in hexane (0.26 ml, 0.416 mmol) at -78° . Then a soln. of **12** (120 mg, 0.404 mmol) in THF (5 ml) was added dropwise. After 1.5 h, the mixture was warmed to r.t., and a sat. NH₄Cl soln. (6 ml) and CH₂Cl₂ (35 ml) were added. The org. phase was washed with H₂O, evaporated, and chromatographed (silica gel, hexane/AcOEt 10:1): 131 mg (75%) of **5**. M.p. 109°. IR (KBr): 3066, 2963, 2908, 1670, 1583, 1446, 435, 1397, 1374, 1293, 1258, 1124, 1030, 802, 731, 680, 640, 469. ¹H-NMR (300.13 MHz): 1.76 (*s*, Me); 1.84 (*s*, Me); 1.85 (*s*, Me); 1.87 (*s*, Me); 1.89 (*s*, Me); 3.56 (*d*, J = 2.1, 1 CH (Cp)); 3.63 (*d*, J = 2.1, 1 CH (Cp)); 4.21 (*s*, 1 CH (Cp)); 6.16 (*s*, $S_2C=CH$); 7.3–7.0 (complex *m*, 4 arom. H). ¹³C-NMR (75.47 MHz): 9.1 (Me); 10.0 (Me); 10.1 (Me); 11.5 (Me); 11.7 (Me); 12.3 (Me); 66.9 (CH (Cp)); 69.5 (CH (Cp)); 69.6 (CH (Cp)); 79.1 (CH–*C* (Cp)); 80.0 (MeC (Cp)); 81.1 (MeC (Cp)); 81.7 (MeC (Cp)); 82.1 (MeC (Cp)); 82.5 (MeC (Cp)); 82.7 (MeC (Cp)); 111.3 ($S_2C=CH$); 120.6 (arom. CH); 121.3 (arom. CH); 124.4 ($S_2C=CH$); 125.0 (arom. CH); 125.3 (arom. CH); 135.3 (arom. C–S); EI-MS: 434 (100, M^+); 420, 303, 271, 237, 217, 196, 161, 119, 105. Anal. cale. for $C_{xH}_{H_x}_{Fe}_{S_2}$ (434.4): C 66.35, H 6.28, S 14.76; found: C 66.58, H 6.28, S 14.55.

rac-*1*-[*1*-(*1*,3-Benzodithiol-2-ylidene)-2-oxomethyl]-2,2',3,3',4,4'-hexamethylferrocene (**13**). A mixture of **5** (138.4 mg, 0.318 mmol), POCl₃ (0.03 ml, 0.329 mmol), and DMF (1.5 ml, 19.5 mmol) was stirred overnight. The resulting dark mixture was cooled to 0° and mixed with a NaOAc soln. After 2 h, the product was extracted (CH₂Cl₂, 2N HCl, NaHCO₃, and brine), the org. phase evaporated, and the residue chromatographed (silica gel, hexane/AcOEt 10:1): 85 mg (58%) of **13**. M.p. 131°. IR (KBr): 3068, 2963, 2941, 2903, 2853, 1622, 1452, 1436, 1398, 1206, 1027, 737, 659, 576, 472. ¹H-NMR: 1.72 (*s*, Me); 1.78 (*s*, Me); 1.79 (*s*, Me); 1.82 (*s*, Me); 1.86 (*s*, Me); 1.90 (*s*, Me); 3.68 (*d*, *J* = 2.5, 1 CH (Cp)); 3.81 (*s*, 1 CH (Cp)); 3.83 (*d*, *J* = 2.5, 1 CH (Cp)); 7.6 – 7.2 (complex *m*, 4 arom. H); 10.06 (*s*, CHO). ¹³C-NMR: 8.99 (Me); 9.63 (Me); 11.03 (Me); 11.36 (Me); 11.51 (Me); 12.15 (Me); 68.52 (CH (Cp)); 82.51 (2 MeC (Cp)); 117.396 (S₂C=*C*); 121.42 (arom. CH); 122.67 (arom. CH); 126.19 (arom. CH); 126.31 (arom. CH); 132.87 (arom. C-S); 138.81 (arom. C-S); 158.26 (S₂C=C); 87.97 (CHO). EI-MS: 462 (100, *M*⁺⁺), 355, 270. Anal. calc. for C₂₅H₂₆FeOS₂ (462.5): C 64.93, H 5.67; found: C 65.03, H 5.74.

rac-*1-[1,2-Bis(1,3-benzodithiol-2-ylidene)ethyl]-2,2',3,3',4,4'-hexamethylferrocene* (14). As described for 5, with 18a (111 mg, 0.42 mmol), THF (10 ml), 1.6M BuLi in hexane (0.28 ml, 0.45 mmol), and 13 (128 mg, 0.28 mmol): 146 mg (87%) of 14, after chromatography (silica gel, hexane/AcOEt 20:1). ¹H-NMR: 1.70 (*s*, Me); 1.78 (*s*, Me); 1.79 (*s*, Me); 1.80 (*s*, Me); 1.86 (*s*, Me); 1.84 (*s*, Me); 3.77 (*d*, J=2.2, 1 CH (Cp)); 3.94 (*d*, J=2.2, 1 CH (Cp)); 4.03 (*s*, 1 CH (Cp)); 6.40 (*s*, $_{2}C$ =C-CH=CS₂); 7.3-7.0 (complex *m*, 8 arom. CH). ¹³C-NMR: 9.00 (Me); 9.51 (Me); 11.36 (Me); 11.43 (Me); 11.62 (Me); 12.11 (Me); 67.66 (CH (Cp)); 68.58 (CH (Cp)); 69.40 (CH (Cp)); 80.93 (MeC); 81.74 (MeC); 82.27 (MeC); 82.49 (MeC); 83.92 (MeC); 11.66, 120.22 ($_{2}C$ =C-CH=CS₂); 121.23 (arom. CH); 121.36 (arom. CH); 125.64 (arom. CH); 125.17 (arom. CH); 125.55 (arom. CH); 125.39 (arom. CH); 125.85 (arom. CH); 126.64 (arom. CH); 130.43 ($_{3}C$ =C-CH=CS₂); 133.83 (arom. C-S); 135.51 (arom. C-S); 136.85 (arom. C-S); 137.26 (arom. C-S). EI-MS: 462 (100, *M*⁺). 355, 270. Anal. calc. for $C_{2}H_{30}$ FeS₄ (598.7): C 64.20, H 5.05; found: C 64.31, H 5.21.

1,1'-Diformyl-2,2',3,3',4,4'-hexamethylferrocene (mixture of diastereoisomers; **15**). A mixture of **11** (200 mg, 0.740 mmol), freshyl distilled TMEDA (0.28 ml, 1.87 mmol), and 1.6M BuLi in hexane (1.1 ml, 1.76 mmol) was stirred overnight in hexane (10 ml). The resulting orange soln. was slowly added dropwise to a soln. of DMF (0.13 ml, 1.69 mmol) in Et₂O (2 ml). After additional 20 min, 2N HCl (8 ml) was added. The red org. phase was evaporated and the residue chromatographed (silica gel, hexane/AcOEt 3 :1): 6 mg (2.5%) of **15**. ¹H-NMR: 1.59 (*s*, 2 Me); 1.81 (*s*, 2 Me); 1.88 (*s*, 2 Me); 1.89 (*s*, 2 Me); 2.03 (*s*, 2 Me); 2.04 (*s*, 2 Me); 4.29 (*s*, 2 CH (Cp)); 4.31 (*s*, 2 CH (Cp)); 9.88 (*s*, 2 CHO); 9.91 (*s*, 2 CHO). IR (KBr): 3089, 2955, 2913, 1657, 1446, 1415, 1385, 1364, 1158, 1073, 1033, 829, 722, 651, 624, 510, 465.

1,1',2,2',3,3'-Hexamethyl-4,4'-trithioferrocene (four stereoisomers; **16**). To a mixture of **11** (200 mg, 0.739 mmol) and 1.6M BuLi in hexane (1 ml, 1.6 mmol), freshly distilled TMEDA (0.27 ml, 1.78 mmol) was added dropwise and the resulting mixture stirred overnight. The solvent ws evaporated and the residue dissolved in THF (2 ml). This soln. was transferred to a suspension of sulfur (145 mg, 4.53 mmol) in THF (10 ml). The resulting dark mixture was refluxed overnight and then evaporated and the residue chromatographed (silica gel, hexane): 9 mg (4%) of **16**. M.p. 114°. IR (KBr): 2966, 2987, 1635, 1470, 1442, 1374, 1298, 1123, 1025, 826, 815, 484, 473. ¹H-NMR: 4.17 (*s*, 2 CH (Cp)); 3.52 (*s*, 2 CH (Cp)); 3.48 (*s*, 2 CH (Cp)); 2.89 (*s*, 2 CH (Cp)); 1.81–1.1 (all Me). EI-MS: 364 (100, M^{++}), 331, 300, 258, 241, 209, 192, 182, 138, 105.

[(1,3-Benzodiihiol-2-ylidene)methyl]ferrocene (**19a**). As described for **5** with **18a** (3.67 g, 14 mmol), THF (70 ml), 1.6M BuLi in hexane (8.75 ml, 14 mmol), and formylferrocene (**17**; 2 g, 9.3 mmol) in THF (50 ml): 3.5 g (quant.) of **19a**. M.p. 154°. IR (KBr): 3091, 1588, 1446, 1102, 1031, 807, 745, 503. ¹H-NMR: 4.21 (*s*, 5 CH (Cp)); 4.27 (*m*, J = 1.87, 2 CH (Cp)); 4.46 (*m*, J = 1.87, 2 CH (Cp)); 6.2 (*s*, S₂C=CH); 7.11–7.29 (complex *m*, 4 arom. CH). ¹³C-NMR: 67.79 (CH (Cp)); 68.77 (CH (Cp)); 69.51 (CH (Cp)); 83.12 (CH–C (Cp)); 112.41 (S₂C=CH); 121.36 (arom. CH); 121.99 (arom. CH); 125.82 (arom. CH); 126.14 (arom. CH); 127.96

 $(S_2C=CH)$; 135.91 (arom. C-S); 137.35 (arom. C-S). EI-MS: 350 (100, M^+), 229, 197, 120. Anal. calc. for $C_{18}H_{14}FeS_2$ (434.4): C 61.72, H 4.03, S 18.31; found: C 61.47, H 4.25, S 18.04.

[(5,6-Dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene)methyl]ferrocene (19b). As described for **5**, with dimethyl (5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-yl)phosphonate [20][51][52] (18b; 848 mg, 2.8 mmol), THF (50 ml), 1.6M BuLi in hexane (1.75 ml, 2.8 mmol), and **17** (0.5 g, 2.3 mmol) in THF (25 ml): 0.89 g (98%) of **19b**, after chromatography (silica gel, hexane AcOEt 4:1). M.p. 160°. IR (KBr): 3090, 3000, 2976, 2909, 1583, 1287, 1104, 999, 810, 704, 646, 492, 464. ¹H-NMR: 3.32 (*s*, 2 CH₂); 4.16 (*s*, 5 CH (Cp)); 4.22 (*m*, *J* = 1.88, 2 CH (Cp)); 4.35 (*m*, *J* = 1.88, 2 CH (Cp)); 6.15 (*s*, S₂C=CH). ¹³C-NMR: 30.09 (CH₂); 30.20 (CH₂); 67.71 (CH (Cp)); 68.88 (CH (Cp)); 69.5 (CH (Cp)); 82.73 (CH-*C* (Cp)); 111.29 (CS₂); 111.49 (CS₂); 113.17 (S₂C=*C*H); 125.46 (CS₂). EI-MS: 390 (100, *M*⁺⁺), 362, 269, 242. Anal. calc. for C₁₆H₁₄FeS₄ (390.4): C 49.23, H 3.61, S 32.85; found: C 49.28, H 3.66, S 32.67.

[1-(1,3-Benzodithiol-2-ylidene)-2-oxoethyl]ferrocene (**20a**). As described for **13**, with DMF (20 ml), POCl₃ (0.81 ml, 1.34 g, 8.7 mmol), **19a** (2.96 g, 8.4 mmol), and NaOAc soln. (4.75 ml, 1.5 g \cdot ml⁻¹): 2.87 g (90%) of **20a**. Dark red crystals. M.p. 149°. IR (KBr): 1633, 1494, 1268, 1113, 1047, 1001, 737, 500. ¹H-NMR: 4.24 (*s*, 5 CH (Cp)); 4.41 (*m*, *J* = 1.86, 2 CH (Cp)); 4.58 (*m*, *J* = 1.87, 2 CH (Cp)); 7.28–7.36 (complex *m*, 2 arom. CH); 7.51–7.62 (complex *m*, 2 arom. CH); 9.96 (*s*, CHO). ¹³C-NMR: 67.99 (CH (Cp)); 68.70 (CH (Cp)); 69.74 (CH (Cp)); 84.08 (CH(O)C-C (Cp)); 118.35 (S₂C=C); 121.96 (arom. CH); 123.02 (arom. CH); 126.82 (arom. CH); 126.87 (arom. CH); 133.75 (arom. C–S); 138.89 (arom. C–S); 155.25 (S₂C=C); 186.73 (CHO). EI-MS: (100, *M*⁺⁺), 313, 251, 197, 153. Anal. calc. for C₁₉H₁₄FeOS₂ (378.3): C 60.34, H 3.70; found: C 60.32, H 3.84.

[1-(5,6-Dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene)-2-oxoethyl]ferrocene (**20b**). As described for **13**, with DMF (3 ml), oxalyl chloride (220 µl, 325 mg, 2.56 mmol), **19b** (500 mg, 1.28 mmol), and sat. NaOAc soln. (5 ml). 476 mg (89%) of **20b**, after recrystallization from 1,2-dichloroethane as thin orange needles. M.p. 240° (dec). IR (KBr): 3090, 2964, 2924, 2836, 1614, 2527, 1486, 1421, 1376, 1350, 1274, 1205, 1173, 1119, 1105, 1042, 998, 925, 892, 827, 809, 663, 598, 568, 504, 488, 476, 434. ¹H-NMR: 3.37 (*s*, SCH₂CH₂S); 4.20 (*s*, 5 CH (Cp)); 4.35 (*m*, *J* = 2.00, 2 CH (Cp)); 4.50 (*m*, *J* = 2.00 Hz, 2 CH (Cp)); 9.78 (*s*, CHO). ¹³C-NMR (75.467 MHz): 28.6 (SCH₂); 28.8 (SCH₂); 66.7 (CH (Cp)); 67.9 (CH (Cp)); 69.0 (CH (Cp)); 76.9 (CH(O)C-*C* (Cp)); 83.3, 184.5 (CHO). EI-MS: 418 (100, *M*⁺⁺), 390, 325, 270, 242, 205, 121. Anal. calc. for C₁₇H₁₄FeOS₄ (418.4): C 48.80, H3.37, S 30.66; found: C 48.76, H 3.45, S30.54.

[*1*,2-*Bis*(*1*,3-*benzodithiol*-2-*ylidene*)*ethyl*]*ferrocene* (**21a**). As described for **5**, with **18a** (523 mg, 1.98 mmol), THF (70 ml) 1.6M BuLi in hexane (1.3 ml, 2.08 mmol), **20a** (506 mg, 1.32 mmol), and THF (50 ml): 556 mg (82%) of **21a**, after chromatography (silica gel, hexane/AcOEt 3 :1) and recrystallization from hexane. M.p. 90°. IR (KBr): 3053, 2920, 1569, 1541, 1447, 1432, 1121, 1105, 1029, 1000, 818, 739, 496. ¹H-NMR: 4.24 (*s*, 5 CH (Cp)); 4.28 (*m*, J = 1.9, 2 CH (Cp)); 4.57 (*m*, J = 1.9, 2 CH (Cp)); 6.18 (*s*, $S_2C=C-CH=CS_2$); 7.05 – 7.32 (complex *m*, 8 arom. CH). ¹³C-NMR: 67.83 (CH (Cp)); 68.69 (CH (Cp)); 69.67 (CH (Cp)); 84.19 (CH(=C)C-C (Cp)); 114.81 (S₂C=C-CH=CS₂); 119.84 (S₂C=C-CH=CS₂); 121.62 (arom. CH); 125.98 (arom. CH); 125.98 (arom. CH); 125.96 (arom. CS); 136.7 (arom. C-S); 137.24 (arom. C-S); 137.31 (arom. C-S); 137.71 (S₂C=C). EI-MS: 514 (100, M^{++}), 359, 327, 253, 221. Anal. calc. for C₂₆H₁₈FeS₄ (514.5): C 60.69, H 3.53, S 24.93; found: C 60.98, H 3.93, S 23.91.

[1-(1,3-Benzodithiol-2-ylidene)-2-(5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene)ethyl]ferrocene (**21b**). As described for **5**, with **18b** (600 mg, 1.98 mmol), THF (70 ml), 1.6M BuLi in hexane (1.3 ml, 2.08 mmol), **20a** (502 mg, 1.32 mmol), and THF (50 ml): 452 mg (62%) of **21b**, after chromatography (silica gel, hexane/AcOEt 4:1). M.p. 171°. IR (KBr): 3053, 2920, 1569, 1541, 1447, 1287, 1260, 1121, 1105, 1029, 1000, 818, 739, 496. ¹H-NMR: 3.29 (*s*, SCH₂CH₂S); 4.22 (*s*, 5 CH (Cp)); 4.27 (*m*, *J* = 1.9, 2 CH (Cp)); 4.53 (*m*, *J* = 1.9, 2 CH (Cp)); 6.16 (*s*, S₂C=C-CH=CS₂); 7.09-7.14 (complex *m*, 2 arom. CH); 7.25-7.31 (complex *m*, 2 arom. CH). ¹³C-NMR: 30.12 (SCH₂); 67.97 (CH (Cp)); 68.69 (CH (Cp)); 69.66 (CH (Cp)); 84.12 (CH(=C)C-C (Cp)); 110.61, 112.95, 115.50, 119.51, 121.66 (arom. CH); 121.94 (arom. CH); 125.75 (arom. CH); 125.99 (arom. CH); 129.17, 134.49, 136.6, 137.64. EI-MS: 554 (100, M^+), 514, 438, 172, 108. Anal. calc. for C₂₄H₁₈FeS₆ (554.6): C 51.97, H 3.27, S 34.69; found: C 52.13, H 3.37, S 34.41.

[1,2-Bis(5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene)ethyl]ferrocene (21c). As described for 5, with 18b (162 mg, 0.54 mmol), THF (15 ml), 1.6M BuLi in hexane (0.33 ml, 0.54 mmol), and 20b (150 mg, 0.35 mmol): 150 mg (72%) of 21c, after chromatography (silica gel, AcOEt/hexane/CH₂Cl₂ 10:2:5). M.p. *ca*. 180° (dec.). IR (KBr): 3081, 2917, 1560, 1521, 1409, 1285, 1257, 1105, 1021, 1001, 917, 883, 819, 790, 679, 601, 493. ¹H-NMR: 3.30 (s, 4 H, SCH₂CH₂S); 3.34 (s, 4 H, SCH₂CH₂S); 4.20 (s, 5 CH (Cp)); 4.24 (m, J = 1.7, 2 CH (Cp)); 6.08 (s, S₂C=C-CH=CS₂). ¹³C-NMR (75.467 MHz, 25°): 29.2 (SCH₂); 29.3

 (SCH_2) ; 29.4 (SCH_2) ; 67.0 (CH (Cp)); 68.0 (CH (Cp)); 68.9 (CH (Cp)); 83.1 CH(=C)C-C (Cp); 110.1, 118.8, 112.4, 114.2 $(S_2C=C-CH=CS_2)$; 119.1, 125.9, 134.0. EI-MS: 594 $(10, M^{++})$, 566, 538, 446, 416, 403, 330, 300 (100), 150. Anal. calc. for $C_{22}H_{18}FeS_8$ (594.7): C 44.43, H 3.05; found: C 44.38, H 3.01.

[2-(1,3-Benzodithiol-2-ylidene)-1-(5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene)ethyl]ferrocene (21d). As described for **5**, with **18a** (141 mg, 1.98 mmol), THF (15 ml), 1.6M BuLi in hexane (0.33 ml, 0.54 mmol), and **20b** (150 mg, 0.35 mmol): 75 mg (39%) of **21d**, after chromatography (silica gel, AcOEt/hexane/CH₂Cl₂ 10:2:5). M.p. 109°. IR (KBr): 3088, 2918, 1571, 1551, 1508, 1447, 1432, 1410, 1287, 1260, 1121, 1105, 1030, 1000, 919, 884, 819, 742, 677, 604, 495. 'H-NMR: 3.33 (s, SCH₂CH₂S); 4.22 (s, 5 CH (Cp)); 4.25 (m, J = 1.7, 2 CH (Cp)); 4.50 (m, J = 1.7, 2 CH (Cp)); 6.10 (s, S_2 =C-CH=CS₂); 7.0-7.2 (complex m, arom. CH). ¹³C-NMR (75.467 MHz): 29.2 (SCH₂); 29.3 (SCH₂); 67.0 (CH (Cp)); 68.9 (CH (Cp)); 83.1 (CH(=C)C-C (Cp)); 11.6, 112.4, 113.5 (S_2 C=C-CH=CS₂); 119.4, 121.0 (arom. CH); 121.4 (arom. CH); 125.2 (arom. CH); 125.2, (arom. CH); 125.7, 135.2, 136.6, 136.7. EI-MS: 554 (20, M^+), 526, 419, 390, 270, 242, 205, 121 (100). Anal. calc. for C₂₄H₁₈FeS₆ (554.6): C 51.97, H 3.27; found: C 52.64, H 3.62.

1,1'-Bis[*1-(1,3-benzodithiol-2-ylidene)-2-oxoethyl]ferrocene* (**23a**). As described for **13**, with DMF (17 ml), POCl₃ (0.2 ml, 0.34 g, 2.22 mmol), 1,1'-bis[(1,3-benzodithiol-2-yliden)methyl]ferrocene [2] (**22a**; 0.567 g, 1.1 mmol), and a NaOAc soln. (17 ml, 3 g in 20 ml of H₂O): 0.44 g (71%) of **23a**, after recrystallization from 1,2-dichloroethane. IR (KBr): 3073, 2836, 1632, 1491, 1478, 1272, 1112, 740, 505. ¹H-NMR: 4.44 (m, J = 1.8, 4 CH (Cp)); 4.68 (m, J = 1.8, 4 CH (Cp)); 7.15 – 7.28 (complex m, 4 arom. CH); 7.42 – 7.54 (complex m, 4 arom. CH); 9.78 (s, 2 CHO). ¹³C-NMR: 68.23 (CH (Cp)); 69.33 (CH (Cp)); 85.08 (CH(O)C–C (Cp)); 116.50 (S₂C=C); 121.47 (arom. CH); 122.46 (arom. CH); 126.24 (arom. CH); 126.31 (arom. CH); 138.35 (arom. C–S); 185.24 (CHO). EI-MS: 570 (100, M^{++}), 313, 197. Anal. calc. for C₂₈H₁₈FeO₂S₄ (570.5): C 58.94, H 3.18, S 22.48; found: C 59.10, H 3.13, S 22.63.

1,1'-Bis[*1,2-bis*(*1,3-benzodithiol-2-ylidene*)*ethyl*]*ferrocene* (**6a**). As described for **5**, with **18a** (0.602 g, 2.6 mmol), THF (50 ml), 1.6M BuLi in hexane (1.44 ml, 2.30 mmol), and **23a** (0.44 g, 0.76 mmol) suspended in THF (150 ml): 0.56 g (88%) of **6a**, after chromatography (silica gel, CH₂Cl₂). M.p. 223° (dec.). IR (KBr): 3053, 2987, 1570, 1536, 1447, 1433, 1122, 735, 502, 476. ¹H-NMR: 4.37 (m, J = 1.7, 4 H, Cp); 4.62 (m, J = 1.7, 4 H, Cp); 6.17 (s, 2 S₂C=C-CH=CS₂); 6.99-7.21 (complex m, 16 arom. CH). ¹³C-NMR: 68.62 (CH (Cp)); 69.44 (CH (Cp)); 84.76 (CH(=C)C-C (Cp)); 114.5 (S₂C=C-CH=C(S₂)); 118.43, 121.07 (arom. CH); 121.18 (arom. CH); 121.54 (arom. CH); 121.64 (arom. CH); 125.47 (arom. CH); 125.40 (arom. CH); 125.46 (arom. CH); 129.22, 135.55, 136.19, 136.65, 137.01, 137.28. EI-MS: 842 (20, M^{++}), 394, 303, 217 (100), 184, 110. Anal. calc. for C₄/H₂₆FeS₈ (843.0): C 59.84, H 3.11; found: C 59.71, H 2.95.

1,1'-Bis[*1-(1,3-benzodithiol-2-ylidene)-2-(5,6-dihydro-1,3-dithiolo*[*4,5-b*][*1,4*]*dithiin-2-ylidene)ethyl*]*ferrocene* (**6b**). As described for **5**, with **18b** (0.625 g, 2.07 mmol), THF (50 ml), 1,6M BuLi in hexane (1.29 ml, 2.06 mmol) and **23a** (0.4g, 0.69 mmol) suspended in THF (100 ml): 0.375 g (76%) of **6b**, after two recrystallizations, first from 1,2-dichloroethane, and second from benzene. M.p. 181° (dec.). IR (KBr): 3432, 2907, 1564, 1512, 1448, 1279, 1256, 1122, 1023, 952, 738, 494. ¹H-NMR: 3.29 (*s*, 2 SCH₂CH₂S); 4.35 (*m*, *J* = 1.7, 4 H, Cp); 4.57 (*m*, *J* = 1.7, 4 H, Cp); 6.13 (*s*, S₂C=C-CH=C(S₂)); 7.01-7.23 (complex *m*, 8 arom. CH). ¹³C-NMR: 30.14 (SCH₂); 69.15 (CH (Cp)); 69.78 (CH (Cp)); 85.05 (CH(=C)C-C (Cp)); 110.71, 113.11, 115.66, 118.37, 121.54 (arom. CH); 121.96 (arom. CH); 125.63 (arom. CH); 125.83 (arom. CH); 129.85, 134.2, 136.51, 137.68. FAB-MS: 922 (100, *M*⁺⁺), 766, 391. Anal. calc. for C₃₈H₂₆FeS₁₂ (923.2): C 49.44, H 2.84; found: C 48.78, H 3.07.

Charge-Transfer Complexes with $[M(mnt)_2]^-$ (M = Ni, Pt): General Procedure (GP), Exemplified by the Synthesis of meso-1,1'-Bis[(tert-butyl)thio]-2,2',3,3',4,4'-hexamethylferrocenium Bis[2,3-di(mercapto- κ S)but-2-enedinitrilato(2⁻)]nickelate(1⁻) ([meso-Fe[η ⁵-C₃Me₃(S'Bu)]₂][Ni(mnt)₂]; **26**). meso-Enriched **3a** (103 mg, 0.23 mmol; mesolrac 85:15) and ferrocenium bis[2,3-di(mercapto- κ S)but-2-enedinitrilato(1⁻)]nickelate(1⁻) ([FeCp₂][Ni(mnt)₂]; **24**; 104 mg, 0.20 mmol) were refluxed in MeCN. Then the mixture was evaporated and the residue recrystallized from AcOEt: 116 mg (64%) of **26**. Black needles. Single crystals were obtained by slow diffusion of hexane into a sat. soln. of the salt in CH₂Cl₂. IR (KBr): 3107, 2923, 2207, 1632, 1416, 1160, 1009, 855, 502. Anal. calc. for C₃₂H₃₈FeN₄NiS₆ (785.6): C 48.92, H 4.88, N 7.13; found: C 49.06, H 4.92, N 7.09.

meso-1,1'-Bis[(tert-butyl)thio]-2,2',3,3',4,4'-hexamethylferrocenium Bis[2,3-di(mercapto-κS)but-2-enedinitrilato(2 –)]platinate(1 –) ([meso-Fe{ η^5 -C₅Me₃(S'Bu)]₂][Pt(mnt)₂]; **27**). According to the *GP*, from ferrocenium bis[2,3-di(mercapto-κS)but-2-enedinitrilato(1 –)]platinate(1 –) ([FeCp₂][Pt(mnt)₂]; **25**; 110 mg, 0.17 mmol) and meso-enriched **3a** (74 mg, 0.17 mmol; meso/rac 94 : 6). 79 mg (52%) of **27**. Black powder. Single crystals were obtained by slow diffusion of Et₂O into a sat. soln. of the salt in CH₂Cl₂. IR (KBr): 3070, 2961, 2922, 2210, 1445, 1364, 1162, 1017, 878, 570, 527, 360, 212. Anal. calc. for C₃₂H₃₈FeN₄PtS₆ (922.0): C 41.69, H 4.15, N 6.08; found: C 41.78, H 4.32, N 6.08. 1,1',2,2',3,3',4,4'-Octamethyl-5,5'-trithioferrocenium Bis[2,3-di(mercapto-κS)-but-2-enedinitrilato(2 –)]nickelate(1 –) ([Fe(η^5 -C₃Me₄S)₂S][Ni(mnt)₂]; **28**). According to the *GP*, from [Fe{(η^5 -C₃Me₄S)₂S]] (**4**; 100 mg, 0.25 mmol) and **24** (134 mg, 0.25 mmol): 131 mg (72%) of **28**. Dec. > 260°. Single crystals were obtained by slow diffusion of 'BuOME into a sat. soln. of the salt in MeCN. IR (KBr): 2959, 2917, 2207, 1448, 1379, 1160, 1019, 524, 501, 400, 367. Anal. calc. for C₂₆H₂₄FeN₄NiS₇ (731.5): C 42.69, H 3.31, N 7.66; found: C 42.67, H 3.11, N 7.55.

1,1',2,2',3,3',4,4'-Octamethyl-5,5'-trithioferrocenium Bis[2,3-di(mercapto-κS)-but-2-enedinitrilato(2 –)]platinate ([Fe(η^5 -C₅Me₄S)₂S][Pt(mnt)₂]; **29**). According to the *GP*, from [Fe{(η^5 -C₅Me₄S)₂S]] (**4**) (80 mg, 0.24 mmol) and **25** (157 mg, 0.24 mmol): 124 mg (63%) of **29**. Dec. > 260°. IR (KBr): 2960, 2919, 2208, 1448, 1378, 1162, 1019, 524, 500, 384, 354, 328. Anal. calc. for C₂₆H₂₄FeN₄PtS₇ (867.9): C 35.98, H 2.79, N 6.46; found: C 36.04, H 2.90, N 6.44.

rac-*I*-[(1,3-Benzodithiol-2-ylidene)methyl]-2,2',3,3'-4,4'-hexamethylferrocenium Bis[2,3-di(mercapto-κS)but-2-enedinitrilato(2 –)]nickelate(1 –) 1,2-Dichloroethane Adduct (**30**). According to the *GP*, from **5** (30 mg, 0.069 mmol) and **24** (36.2 mg, 0.69 mmol): 36 mg (60%) of **30**, after recrystallization from 1,2-dichloroethane/hexane. Black powder. Dec. > 240°. Single crystals were obtained by slow diffusion of hexane into a sat. soln. of the salt in 1,2-dichloroethane. IR (KBr): 1916, 2206, 1566, 1528, 1381, 1340, 1159, 1019, 946, 832, 805, 734, 678, 641, 518, 501, 366. Anal. calc. for $C_{34}H_{30}Cl_2FeN_4NiS_6$ (872.5): C 46.81, H 3.47, N 6.42; found: C 46.91, H 3.17, N 6.40.

1,1'Bis[*1,2-bis*(*1,3-benzodithiol-2-ylidene*)*ethyl*]*ferrocenium Bis*[*2,3-di*(*mercapto-κ*S)*but-2-enedinitrilato-*(*2–*)*]nickelate*(*1–*) (**31**). According to the *GP*, from **6a** (50 mg, 0.059 mmol) and **24** (31 mg, 0.059 mmol) in 1,2-dichloroethane (5 ml) and MeCN (3 ml) by slow diffusion of hexane into this filtered soln. 32 mg (45%) of **31**. Very thin black needles. IR (KBr): 2206, 1569, 1539, 1473, 1453, 1435, 1377, 1291, 1203, 1159, 1120, 1055, 833, 740, 678, 631, 465. Anal. calc. for $C_{50}H_{26}FeN_4NiS_{12}$ (1182.1): C 50.80, H 2.22, N 4.74; found: C 51.29, H 2.18, N 4.78.

1,1'-Bis[*1,2-bis*(*1,3-benzodithiol-2-ylidene)ethyl*]*ferrocenium Bis*[*2,3-di*(*mercapto-κ*S)*but-2-enedinitrilato-*(*2–*)*Jnickelate*(*1–*) *1,2-Dichloroethane Adduct* (**31a**). According to the *GP*, from **6a** (30 mg, 0.042 mmol) and **24** (23 mg, 0.042 mmol) in a minimal amount of 1,2-dichloroethane. Single crystals were obtained by slow diffusion of hexane into this filtered soln.: 23 mg (43%) of **31a** as black plates, together with 22 mg (44%) of **31** as very thin needles. **31a**: IR (Kbr): strong absorption down to 3000, 2204, 1567, 1472, 1401, 1368, 1268, 1207, 1120, 1060, 939, 905, 838, 800, 743, 706, 679, 457. Anal. calc. for $C_{32}H_{30}Cl_2FeN_4NiS_{12}$ (1281.0): C 48.76, H 2.36, N 4.37, S 30.04; found: C 48.95, H 2.58, N 4.39, S 29.76.

1,1'-Bis[1,2-bis(1,3-benzodithiol-2-ylidene)ethyl]ferrocenium Bis[2,3-di(mercapto-κS)but-2-enedinitrilato-(2-)]platinate(1-) (**32**). According to the *GP*, from **6a** (50 mg, 0.06 mmol) and **25** (40 mg, 0.06 mmol) in a minimal amount of 1,2-dichloroethane. The product was obtained by slow diffusion of 'BuOMe into this filtered soln. and recrystallization from 1,2-dichloroethane: 13 mg (27%) of **32**. IR (KBr): 2206, 1567, 1534, 1471, 1453, 1434, 1405, 1372, 1276, 1203, 1162, 1118, 1042, 907, 821, 737, 678, 463. Anal. calc. for C₅₀H₂₆FeN₄PtS₁₂ (1318.4): C 45.55, H 1.99, N 4.25, S 29.18; found: C 45.67, H 1.86, N 4.33, S 28.99.

1,1'-Bis[*1-(1,3-benzodithiol-2-ylidene)-2-(5,6-dihydro-1,3-dithiolo*[*4,5-b*][*1,4*]*dithiin-2-yliden)ethyl*]*ferroce-nium Bis*[*2,3-di(mercapto-κS)but-2-enedinitrilato*(2-)]*nickelate*(1-) (**33**). According to the *GP*, from **6b** (30 mg, 0.042 mmol) and **24** (23 mg, 0.042 mmol) in a minimal amount of 1,2-dichloroethane. The product was obtained by slow diffusion of 'BuOMe into this filtered soln. and recrystallization from 1,2-dichloroethane: 14 mg (31%) of **33**. IR (KBr): 2205, 1420, 1378, 1271, 1200, 1113, 905, 796, 745, 679, 466. Anal. calc. for C₄₆H₂₆FeN₄NiS₁₆ (1262.3): C 43.77, H 2.08, N 4.44; found: C 43.75, H 2.37, N 4.53.

X-Ray Crystallographic Study of **6a,b, 21c,d, 23a, 26–28, 30**, and **31a**. Suitable crystals for an X-ray analysis of all of these compounds were obtained by slow diffusion of an apolar solvent ('BuOMe or hexane) in a sat. soln. of the compounds in a polar solvent (CH₂Cl₂, 1,2-dichloroethane or MeCN). Selected crystallographic and relevant data collection parameters are listed in *Table 2*. Data were measured at r.t. (293(2) K) with 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 direct or *Patterson* methods and refined by full-matrix least squares with anisotropic displacement parameters for all non-H-atoms. The contribution of the H-atoms in their idealized position (riding model with fixed isotropic $U = 0.080 \text{ Å}^2$) was taken into account but not refined. All calculations were carried out with the *Siemens* SHELX93 (VMS) system. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no. CCDC 112681. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223336-033; e-mail: deposit@ccdc.cam.ac.uk).

Magnetic Measurements. The magnetic susceptibility χ of the charge-transfer complexes **26–30** and **31a** was measured in the temp. range of 2–300 K in an external variable magnetic field, by means of a *Quantum-Design* superconducting quantum interference device (SQUID) magnetometer. The polycrystalline samples were mounted in a sample-holder tube made of quartz glass in order to keep the magnetic background as low as possible. Routine corrections for the sample holder were applied.

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