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Electronic Spectra of Ferrocenyldithiolene Nickel Complexes: Steric and Electron Donor/Acceptor Effects[†]

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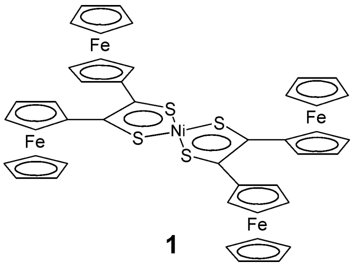
Unlike other dithiolenes, ferrocenyl-substituted dithiolenes show *two* low-energy absorptions of comparable intensity in the 1200 and 750 nm regions. The longest wavelength peak is strongly influenced by electron-donating or -withdrawing groups, whereas the shorter wavelength peak is much less affected. Reducing the overlap between the ferrocene groups and the dithiolenes leads to shifts of both peaks to higher energy. Increased conjugation led to a remarkable shift of the first peak but influences the second one hardly at all. Although several of the results could be used to assign the longest wavelength peak to an Fe → π* transition, we present evidence that it originates from the π system ($\pi \rightarrow \pi$*).

Introduction

By virtue of their low-lying LUMO's, dithiolene complexes are good electron acceptors and show a strong $\pi \rightarrow \pi$* (HOMO−LUMO) transition in the near-IR region. Electron-donating substituents can shift this absorption to lower energies, whereas electron-acceptor substituents have relatively little effect.[1] When we first obtained bis(1,2-diferrocenyldithiolene)nickel (**1**), we noted the large bathochromic shift of the lowest energy transition (LE) to 1310 nm, which we attributed to the electron-donating effect of the ferrocene substituents.[2] A large shift was expected because the dithiolene near-IR (NIR) maximum can be shifted by strong donor substituents up to 1440 nm.



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The $\pi \rightarrow \pi$* transitions of dithiolenes usually are broad, intense near-IR maxima, with ϵ values in the 25 000−40 000 M^{-1} cm^{-1} range.[3] The 1310 nm absorption of **1** was noticeably weaker, with ϵ_{max} only being 10 500 M^{-1}cm^{-1} (Figure 1). The spectrum of **1** also showed a *second* absorption of similar intensity at the edge of the visible region at 772 nm (ϵ_{max} = 8650 M^{-1} cm^{-1}). Because dithiolenes usually show only a very weak d−d transition in the visible region,[4] we considered the appearance of this significant peak at higher energy to be a surprising but, at that time, unexplainable curiosity.

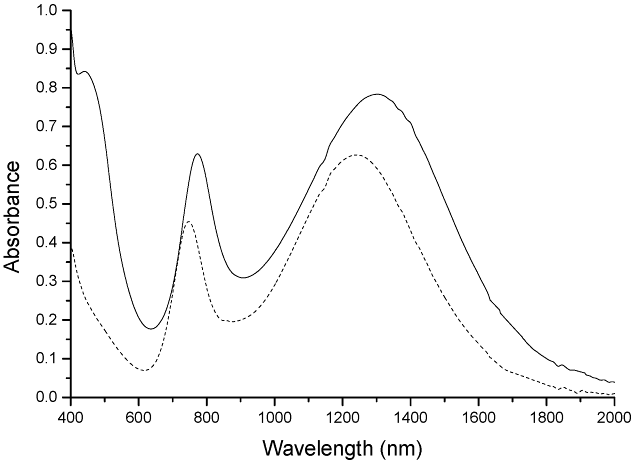

Figure 1. Vis−near-IR spectra of **1** (solid line) and **2** (dashed line) in CH$_2$Cl$_2$.

A possible interpretation comes from the work of Barlow and Marder,[5] who observed two peaks of com-

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[†] U.T.M.-W. wishes to dedicate this publication to Professor Klaus Hafner, Darmstadt, Germany. Taken in part from the Ph.D. thesis of R.W.S., University of Connecticut, 2002.

[‡] Permanent address: U.S. Coast Guard Academy, New London, CT 06320.

(1) Mueller-Westerhoff, U. T.; Vance, B. Dithiolenes and Related Species. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, U.K., 1987; Chapter 16.5, and references therein.

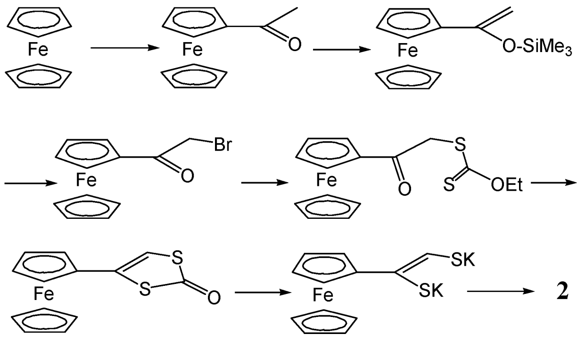
(2) Mueller-Westerhoff, U. T.; Vance, B.; Yoon, D. I. *Tetrahedron* **1991**, *47*, 909.

(3) An exceptionally sharp and much more intense (ϵ = 80 000 M^{-1} cm^{-1}) peak has been observed in a rigid Ni complex: Bigoli, F.; Deplano, P.; Devillanova, F. A.; Lippolis, V.; Lukes, P. J.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *J. Chem. Soc., Chem. Commun.* **1995**, 371. Bigoli, F.; Deplano, P.; Devillanova, F. A.; Ferraro, J. R.; Lippolis, V.; Lukes, P. J.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F.; Williams, J. M. *Inorg. Chem.* **1997**, *36*, 1218. Bigoli, F.; Deplano, P.; Mercuri, M. L.; Pellinghelli, M. A.; Pintus, G.; Trogu, E. F.; Zonnedda, G.; Wang, H. H.; Williams, J. M *Inorg. Chim. Acta* **1998**, *273*, 175.

(4) The usual alkyl- or aryl-substituted square planar dithiolenes of the d^8 metals show a strong $\pi \rightarrow \pi$* transition in the 700−1400 nm range which is subject to predictable substituent effects. No emission from the excited state is observable, because intersystem crossing and internal conversion lead to effective and rapid deactivation. A weak (ϵ < 1000) peak in the 500−600 nm range is a d−d transition: Herman, Z. S.; Kirchner, R. F.; Loew, G. H.; Mueller-Westerhoff, U. T.; Nazzal, A.; Zerner, M. C. *Inorg. Chem.* **1982**, *21*, 46.

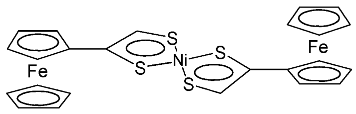
10.1021/om0210053 CCC: $25.00

Scheme 1. Synthesis of Dithiolene 2



parable intensity in several conjugated ferrocene and biferrocene compounds and assigned the lower energy peak (LE) to an electronic transition originating from the iron center (Fe → π^*) and the higher energy peak (HE) to a transition within the π system ($\pi \rightarrow \pi^*$). Recent publications from the same group have confirmed this assignment in other systems as well.[6,7]

We decided to investigate this phenomenon in more detail on complexes of the bis(1-ferrocenyldithiolene) type **2**, especially since two publications[8] by Underhill et al. had provided spectral data for this compound, which did not match what we would have expected (vide infra).



2

Results

The synthesis of **2** used the known[8] intermediate 4-ferrocenyl-1,3-dithiol-2-one (**10**), which was prepared from ferrocene by the route described in Scheme 1. Cleavage by KOH in methanol led to the ethylenedithiolate dianion, and addition of nickel chloride in dilute HCl produced **2** after air oxidation.

The dithiolene **2** was obtained in 13% yield, based on acetylferrocene, as a gray-black microcrystalline solid and was characterized by MS (APCI), NMR (^{1}H and ^{13}C), and near-IR spectra and cyclic voltammetry. The spectral data leave no doubt about the structure of **2**. Its solubility in nonpolar organic solvents, including, in a limited way, hexane, shows that **2** is a neutral dithiolene rather than an anionic species. Although full details of the electrochemistry of **2** will be reported in a different context,[9] it is of interest here that cyclic voltammetry in noncoordinating electrolytes reveals **2** to be a four-electron reservoir[10] with two fully reversible one-electron dithiolene reductions at −0.566 and −1.336 V vs ferrocene and two reversible one-electron oxidations of the ferrocenyl groups at 0.137 and 0.324 V. The fact that the ferrocene oxidation potentials are so widely separated shows a considerable degree of conjugation across the dithiolene.[11]

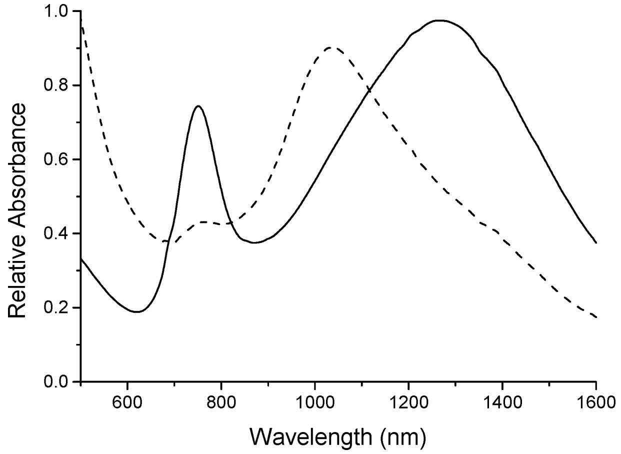


Figure 2. Spectra of **2** in fresh DMF (solid line) and after 4 h (dashed line).

Like the spectrum of **1**, the vis−near-IR spectrum of **2** in dichloromethane shows two major absorptions (Figure 1), one in the near-IR region at 1235 nm (ϵ = 8500 M^{-1} cm^{-1}) and a slightly weaker one at the edge of the visible region at 746 nm (ϵ = 6170 M^{-1} cm^{-1}). In hexane solution, these peaks are shifted to higher energies with $\lambda_{\max}$ 1137 and 735 nm. Although the LE band in appears much broader than its HE counterpart, an energy linear plot (Figure 3) reveals the two peaks to be of comparable width.[12]

The position of the LE transition in either of the above two solvents disagrees with the reported[8] value of 1030 nm. The earlier investigators also made no mention of a second intense peak near 750 nm. We were able to explain these differences through a simple experiment: because DMF, by virtue of the formation of dimethylamine upon standing, acts as a mild reducing agent toward dithiolenes,[13] a solution of **2** in clean DMF will gradually produce the anion **2**$^-$. This reduction is accompanied by a shift of the long-wavelength maximum toward higher energy and a decrease in intensity of the second peak. In Figure 2, the two extremes are documented: initially, **2** was found to absorb in the near-IR region at 1257 nm. After 4 h, the peak had moved to 1032 nm, very close to the reported value of 1030 nm. The second peak did not shift significantly during the reduction, but it became much less intense relative to the first peak and appeared like the usual

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(5) Barlow, S.; Marder, S. R. *Chem. Commun.* **2000**, 1555.

(6) Barlow, S.; Bunting, H. E.; Ringham, C.; Green, J. C.; Bublitz, G. U.; Boxer, S. G.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc.* **1999**, *121*, 3715.

(7) Barlow, S.; Henling, L. M.; Day, M. W.; Schaefer, W. P.; Green, J. C.; Hascall, T.; Marder, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 6285.

(8) Wilkes, S. B.; Butler, I. R.; Underhill, A. E.; Kobayashi, A.; Kobayashi, H. *J. Chem. Soc., Chem. Commun.* **1994**, 54. Underhill, A. E.; Charlton, A.; Wilkes, S. B.; Butler, I. R.; Kobayashi, A.; Kobayashi, H. *Synth. Met.* **1995**, *70*, 1101.

(9) Sommer, R.; Geiger, W. E.; Sanders, R. W.; Mueller-Westerhoff, U. T. Unpublished results.

(10) Compound **1** is a six-electron reservoir with four separate ferrocene oxidations and two distinct dithiolene reductions: Barrière, F.; Camire, N.; Geiger, W. E.; Mueller-Westerhoff, U. T.; Sanders, R. W. *J. Am. Chem. Soc.* **2002**, *124*, 7262.

(11) The second reduction of this complex, $(ML_2)^- \rightarrow (ML_2)^{2-}$, was not observed in the earlier electrochemical analyses by not scanning to sufficiently negative potentials. Only one ferrocene oxidation was reported and erroneously attributed to a two-electron oxidation. This was taken as evidence that "the nickel-bis(dithiolene) core does not serve as an efficient bridge for communication between the two ferrocenyl redox centers".[14]

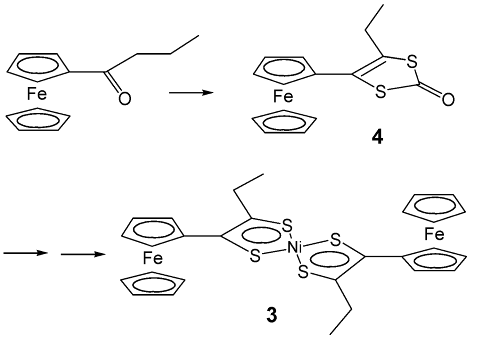
(12) In all known series of dithiolenes with Ni, Pd, and Pt as the central metal, the Pd complex absorbs at the longest wavelength and the Pt complex at the shortest. This trend is followed for the LE peaks *and* for the HE maxima of **2** and its Pd and Pt analogues, independent of solvent polarity (maxima for the Pd complex 1156, 795 nm in hexane and 1281, 818 nm in CH_2Cl_2; maxima for the Pt complex 1072, 707 nm in hexane and 1161, 730 nm in CH_2Cl_2).

(13) Mueller-Westerhoff, U. T. MS thesis, Munich, 1964.

weak d−d transitions of dithiolenes. This easily makes the initial erroneous assignment understandable and confirms the findings of Lee et al.[14] that the earlier work did not deal with the dithiolenes **2** itself but rather with the radical anion $\mathbf{2}^-$.

Ferrocene−Dithiolene Overlap. Because of the sterically not very demanding conditions in dithiolene **2**, the ferrocene Cp rings most likely are in good overlap with the dithiolene π-system: rotation around the C−C bonds connecting the subunits is certainly possible, but to maximize delocalization and overall stability, a coplanar or near-coplanar configuration should be favored.[15] The tetraferrocenyl dithiolene species **1**, on the other hand, is sterically too encumbered to achieve a similar degree of conjugation. Although **1** contains twice the electron-donating ferrocenes as **2**, its LE at 1310 nm and HE at 773 nm (CH_2Cl_2) are only moderately lower in energy compared to compound **2**, whose maxima in CH_2Cl_2 are found at 1235 and 746 nm. The increased donor potential appears reduced by the decrease in effective overlap.

To simplify our analysis, we synthesized dithiolene **3**, in which the ethyl group provides steric encumbrance for the ferrocenyl group without having a major electronic effect itself. The dithiolene precursor **4**, 1-ethyl-2-ferrocenylethylenedithiocarbonate, was prepared from butyrylferrocene by standard methods and cleaved by KOH/MeOH to potassium ethylenedithiolate, which then was reacted with $NiCl_2$ in water under aerobic conditions.



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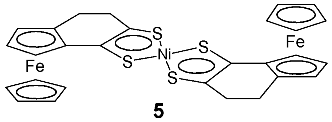
3

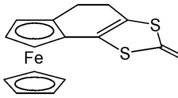
The absorption spectra of **3** were recorded in hexane (1059 and 754 nm) and CH_2Cl_2 (1141 and 762 nm). When the spectra of **2** and **3** (in CH_2Cl_2) are compared, one notes the hypsochromic shift by 94 nm (667 cm^{-1}) of LE and a less pronounced bathochromic shift by 16 nm (247 cm^{-1}) of the second maximum. To weigh the inductive effect of the ethyl group, we can refer to earlier work[16] in which a bathochromic shift of approximately 25 nm per alkyl group was established for the $\pi \rightarrow \pi^*$ transitions of dithiolenes. This tells us that the second peak, regardless of its nature, may experience a modest hypsochromic shift as well (approximately 10 nm), which, however, is more than compensated by the contribution of the ethyl group. That the sterically induced decrease in ferrocene−dithiolene conjugation shifts both maxima to higher energies indicates that the ferrocene Cp ring in the parent complex **2** must be nearly coplanar with the dithiolene.

To substantiate this theory, we wanted to inhibit the rotation around the C−C bond connecting the ferrocenes and dithiolene by adding a carbon bridge between the ortho carbons of ferrocene and dithiolene. Because the introduction of a one-carbon bridge poses many synthetic problems, we prepared the dithiolene **5** with a two-carbon tether.



5

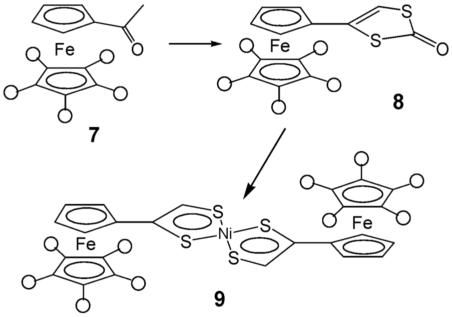
For the synthesis of **5**, ferrocene was acylated under Friedel−Crafts conditions with succinic anhydride to β-ferrocenoylpropionic acid, which was reduced under Clemmensen conditions to γ-ferrocenylbutyric acid, homoannular cyclization of which with trifluoroacetic anhydride yielded 1-keto tetramethylene ferrocene, which was converted to the ethylenedithiocarbonate **6**



6

via formation of the TMS enol ether, bromination, exchange of bromide for xanthate and acid-catalyzed cyclization. Conversion of **6** to the dithiolene **5** followed procedures established for **2**. The spectral data in hexane (1132 and 753 nm) and CH_2Cl_2 solution (1235 and 772 nm) show that the introduction of an ethano tether in **5** has no influence on LE. However, HE is shifted to longer wavelengths than in **2**. Comparison of the HE positions in **5** and **3** shows very little difference and strongly suggests that this shift may be due to the alkyl group.

Electron Donor/Acceptor Effects. To allow a more direct comparison of electron donor effects, **9**, the pentamethylcyclopentadienyl (Cp*) analogue of **2**, was prepared. Our strategy to prepare the intermediate **8** involved initial formation of a Cp*FeCl half-sandwich by addition at −70 °C of Cp*Na to $FeCl_2 \cdot 1.5THF$. Addition of $CH_3CO-CpNa$ led to **7** in 54% yield. The ethylenedithiocarbonate **8** and the dithiolene complex **9** were prepared from **7** via standard procedures.



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8

9

The nickel dithiolene **9** showed absorption maxima at 1395 and 748 nm in hexane and at 1594 and 765 nm in CH_2Cl_2. There exists a significant difference in the bathochromic shifts of the two peaks in CH_2Cl_2 with LE shifted by 359 nm (1823 cm^{-1}) vs HE by 19 nm (333

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(14) Lee, H. J.; Dong-Youn, N. *J. Mater. Chem.* **2000**, *10*, 2171.

(15) Unfortunately, we have no X-ray diffraction data to decide this point because we so far have been unsuccessful, regardless of the central metal, in growing single crystals of **2** of sufficient quality and size for diffraction studies.

(16) Unpublished results of A. Nazzal and U. T. Mueller-Westerhoff, cited in ref 2.

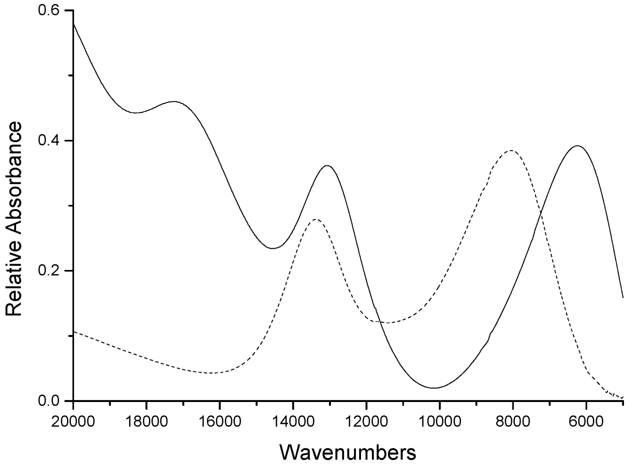


Figure 3. Energy linear plots of the vis−near-IR spectra of **2** (dashed line) and **9** (solid line) in CH_2Cl_2.

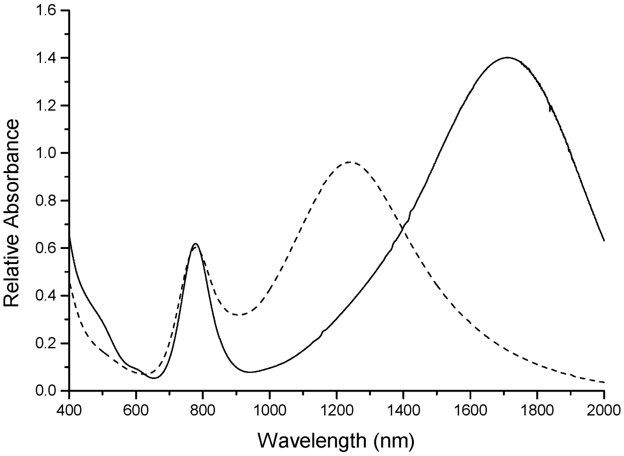
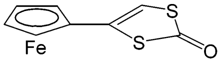


Figure 4. Vis−near-IR spectra of **5** (dashed line) and **14** (solid line) in CH_2Cl_2.

cm^{-1}) from the parent compound **2**. It is worth emphasizing that (a) only LE is strongly affected by enhanced electron donation of the Cp* vs Cp ligands (Figure 3) and (b) the unsubstituted Cp rings can adopt as close to coplanar orientation with the dithiolene core as the parent compound **2**.

To explore the opposite effect, we chose dithiolene **12** containing acetyl groups as typical electron acceptor functions. The ethylenedithiocarbonate **10** was acetylated in excellent yield[17] to produce 4-(1′-acetylferrocenyl)-1,3-dithiole-2-one (**11**). GC-MS and NMR analysis of the acetylated dithiolene revealed that substitution by the electron-withdrawing group occurred solely on the unsubstituted Cp ring. Standard procedures converted **11** to the dithiolene **12** in 32% yield.



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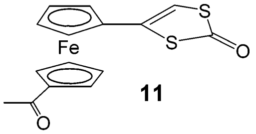

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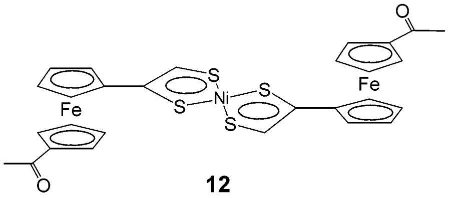

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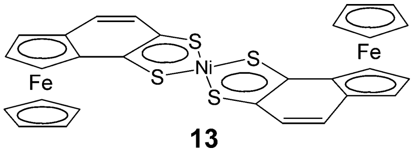
The 1′-acetylferrocenyldithiolene nickel complex **12** showed absorption maxima at 1065 and 726 nm in hexane and at 1114 and 736 nm in CH_2Cl_2. Evidently, the electron acceptor nature of the acetyl groups leads to a noticeable hypsochromic shift compared to **2** of 121 nm (880 cm^{-1}) of LE but only a minor shift (10 nm = 182 cm^{-1}) of HE (in CH_2Cl_2).

Increased Conjugation Effects. Several attempts were made to dehydrogenate the dithiolene **5** to prepare its analogue **13** with two double bonds as the tether. Nearly complete destruction of **5** was observed with a variety of dehydrogenation catalysts. Only some batches of Pd/C in acetone were mild enough to allow a small amount of unsaturated product to be isolated. The near-IR spectrum showed a remarkable bathochromic shift of the LE transition into previously unseen regions and a very small effect on the higher energy peak. The LE and HE values in various solvents are 1513 and 753 nm in hexane, 1721 and 779 nm in dichloromethane, 1653 and 767 nm in ethyl acetate, and 1737 and 774 nm in acetone. Because only a very small amount of product was obtained, the only characterization possible was the APCI mass spectrum, which made it clear that the complex was not **13** but the monounsaturated dithiolene **14**. Even more so, the shift of LE (in CH_2Cl_2) compared to **5** by almost 500 nm (Figure 4) therefore is remarkable.



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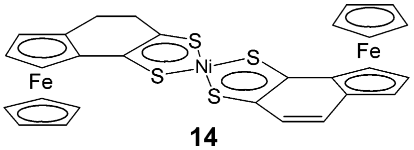

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Influence of Ferrocene Rigidity. The Fe → π* transition relies on overlap between the Fe d AO and the π AO on the adjacent C atom of the dithiolene π system, much like α-ferrocenyl carbenium ions are stabilized by electron donation from the Fe d AO to the vacant p AO of the carbenium carbon atom.[18] For the best interaction, the ferrocene would have to distort to allow the Fe d AO to approach the dithiolene π system as closely as possible. Making the ferrocene more rigid should suppress such distortion and therefore shift the Fe → π* transition to higher energy. To test this idea,

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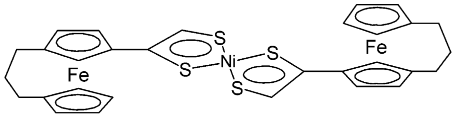
(17) We found (unpublished results) that the related reaction of 1-phenylethylenedithiocarbonate under identical conditions does not lead to a substitution product because the positive change of the dithiocarbonate upon complexation by $AlCl_3$ deactivates the phenyl ring. On the other hand, the Cp rings of ferrocenes are sufficiently independent that substitution of the distant Cp ring in **6** can occur.

(18) Fe−C interactions have been postulated and proven to exist to explain the unusual stability of ferrocenyl α-carbenium ions. A η^6-fulvene type interaction is seen in some, but not all, such cations. Nonetheless, direct Fe to α-C interactions seem to be important in all cases. Some examples for the subtlety of these questions are: Behrens, U. *J. Organomet. Chem.* **1979**, *182*, 89. Mueller-Westerhoff, U. T.; Nazzal, A.; Prössdorf, W.; Mayerle, J. J.; Collins, R. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 293; *Angew. Chem. Suppl.* **1982**, 686−695.

Table 1. Absorption Maxima of Ni Dithiolenes 2, 3, 5, 9, 12, 14, and 15

	peak position						shift vs **2** in hexane			
	in CH_2Cl_2		in hexane							
	LE (nm)	HE (nm)	LE (nm)	HE (nm)	LE (cm^{-1})	HE (cm^{-1})	ΔLE (nm)	ΔHE (nm)	ΔLE (cm^{-1})	ΔHE (cm^{-1})
2	1235	746	1137	735	8795	13 605	0	0	0	0
3	1141	762	1059	754	9443	13 263	−78	19	648	−342
5	1235	772	1132	753	8834	13 280	−5	18	39	−325
9	1594	765	1395	748	7168	13 369	258	13	−1627	−236
12	1114	736	1065	726	9390	13 774	−72	−9	595	169
14	1721	779	1513	753	6609	13 280	376	18	−2186	−325
15	1347	753	1195	717	8368	13 947	58	−18	−427	342

we prepared the dithiolene **15** with a three-carbon bridge between the two Cp rings. Acetylation of [3]-ferrocenophane and separation of the isomer mixture led to 3-acetyl[3]ferrocenophane, which was converted to **15** by the usual methods used for **2**. In comparison to **2**, **15** showed a bathochromic shift of LE (112 nm in CH_2Cl_2) and a hypsochromic shift of HE by 11 nm (Table 1). Considering the donor effect of the alkyl bridges, which produce bathochromic shifts for LE and HE, as shown by dithiolene **9**, the contribution of rigidity to the shift of HE will be larger than the observed 11 nm.



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Conclusions

According to the work of Barlow et al., LE would be an Fe $\rightarrow \pi^*$ transition and HE would involve a transition from the ferrocene Cp ligand π-system to the dithiolene ($\pi \rightarrow \pi^*$). The spectroscopic data, summarized in Table 1 for hexane and dichloromethane as solvents, show that LE experiences significant shifts due to steric and electronic effects as well as solvent polarity, which span the range of 545 nm from 1059 nm (**3** in hexane) to 1721 nm (**14** in CH_2Cl_2) but that HE is shifted only over the comparatively narrow range of 46 nm from 726 nm (**12** in hexane) to 779 nm (**14** in CH_2Cl_2).

It can, of course, be misleading to compare shifts in nanometers when two rather different wavelength regions are involved. Table 1 therefore also shows the shift differences in cm^{-1} as an energy linear measure. Figure 3 shows a comparison of the spectra of **2** and **9** plotted in wavenumbers. Both sets of data agree that LE, varying over the range of 3632 cm^{-1}, shows the expected trends of dithiolene $\pi \rightarrow \pi^*$ transitions. The HE peaks also show these trends, but, with a shift range of 937 cm^{-1}, only close to 25% that of LE.

An application of the Barlow assignment to the dithiolenes would consider as evidence that (1) an Fe $\rightarrow \pi^*$ transition would be more strongly affected by loss of coplanarity between the ferrocene and dithiolene rings than a $\pi \rightarrow \pi^*$ transition: the Fe-to-π AO distance increases rapidly with the twist angle and reduces their overlap, whereas the p−p overlap of adjacent carbons on ferrocene and dithiolene is inversely proportional to the cos^2 of this angle, (2) Cp* ligands make the iron more electron rich and thus a more potent donor, strongly affecting the LE, and (3) an acceptor substituent would conversely diminish this donor potential. That HE as a $\pi \rightarrow \pi^*$ transition is only insignificantly affected by donor or acceptor groups in the distant ring would then have to be explained by the considerable electronic independence of the Cp rings in ferrocenes.

If we, however, assign LE to the $\pi \rightarrow \pi^*$ transition, the observed steric and electronic effects are perfectly in line with all other spectral data of dithiolenes: electron donors induce a large bathochromic shift, and the hypsochromic shift by electron acceptors is much smaller. The steric effects observed in **1** and **2** parallel those in all other substituted dithiolenes.[4] The effect of the ethyl groups in **3** and the ethano bridges in **5** also fits well with other data. The extreme shift of LE when **5** is converted to **14** is strong evidence that it is indeed the $\pi \rightarrow \pi^*$ transition; HE remains almost unchanged, and it is tempting to assign it to an Fe $\rightarrow \pi^*$ transition because there are no real structural changes on going from **5** to **14** and the Fe−dithiolene overlap remains constant. However, with HE also showing comparatively small variations in all the other structural and electronic modifications, we might question whether the HE peaks really are transitions involving Fe d AOs.

These results firmly establish the lowest energy absorptions as the $\pi \rightarrow \pi^*$ transitions of ferrocenyl dithiolenes. Whereas there is no doubt that the assignments of Barlow et al. apply to the systems they studied, they clearly do not apply to dithiolenes, which once more establish themselves as a unique species.

Supporting Information Available: Text and figures giving synthetic procedures and characterization details (including copies of NMR spectra). This material is available free of charge via the Internet at http://pubs.acs.org.

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