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tert-Butyl-Substituted Poly(ferrocenylene persulfides)

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The trithiaferrocenophanes $(RC_5H_3)_2FeS_3$ (where R = *t*-Bu, H) were prepared by dilithiation of the *t*-Bu-substituted ferrocenes followed by treatment with elemental sulfur. *t*-BufcS_3 was obtained as the 1,3,1′-isomer. This chiral compound exists in solution as a 1:1 mixture of conformers by virtue of the relative orientation of the trisulfide strap. The species $(t\text{-}Bu)_2fcS_3$ was obtained as the 1,3,1′,4′-isomer, as established by ^1H NMR measurements and X-ray crystallography. The trisulfides were converted to the polymers $[(RC_5H_3)_2FeS_2]_n$ upon desulfurization with Bu_3P, which was shown by ^{31}P NMR spectroscopy to be converted to Bu_3PS. The rate of this desulfurization increases with the polarity of the reaction solvent. GPC measurements indicated that the *t*-Bu- and $(t\text{-}Bu)_2$-substituted polymers are polydisperse with $M_n = 3700$ ($M_w = 26000$) and $M_n = 2400$ ($M_w = 19000$), respectively. The soluble ferrocenylene persulfide polymers undergo reversible electrochemical oxidation in two steps, separated by 290 mV. The first oxidation potential is similar to that for the trisulfide monomer and is thought to correspond to oxidation of alternating Fe centers. The second oxidation converts the remaining Fe^{II} sites. Reduction of $[(t\text{-}Bu)_2fcS_2]_n$ with $LiBHEt_3$ gave $(t\text{-}Bu)_2fcS_2Li_2$, which can be reoxidized (I_2) to the polymer, sulfurized (S_8) to give the trisulfide, and selenized (Se_8) to give $(t\text{-}Bu)_2fcS_2Se$.

Introduction

Organometallic polymers are of interest because they combine the electronic properties associated with transition metals and the processing advantages of organic polymers. Characteristics routinely associated with transition metals such as multiple oxidation states and magnetism are achieved only in rare organic molecules. On the other hand, the solubility enjoyed by many organic macromolecules is virtually unknown for true inorganic polymers.

Ferrocenes have played a central role in the historical development of the organometallic polymers.[1] Species that have attracted significant attention include poly(vinylferrocene)[2] and polyferrocenylenes,[3] as well as ferrocene-based silanes[4] and siloxanes.[5] In the present paper we report on a polymerization procedure that is applicable to a number of ferrocenes. The precursors to the new polymers are ferrocene trisulfides, sometimes called trithiaferrocenophanes. Ferrocene trisulfide (fcS_3) itself was synthesized by Smart and Davison in 1971.[6] This species is structurally novel, since the S_3 strap prevents free rotation of the two cyclopentadienyl rings. Furthermore, the trisulfide linkage adopts a folded, stereochemically nonrigid conformation that is bistable (eq 1).[7] The barrier to folding of the trisulfide is ca. 80 kJ/mol.[8] The stereodynamics of many permutations of $(C_5H_4)_2FeE_3$ have been examined, e.g. for the cases of E = Se, Te and mixed-chalcogen compounds.[9,10] Chemical reduction affords the dithiolates, which can be complexed to metals[11] or protonated to give the dithiols. The dithiols in turn add to olefins to give addition polymers or teleomers.[12]

(1)

The polymerization reaction examined in this work involves the desulfurization of ferrocene trisulfides. As applied to the parent $(C_5H_4)_2FeS_3$ (fcS_3), this desulfurization produces the insoluble substance fcS_2, which is probably polymeric.[13] The insolubility of fcS_2 has led us to examine families of ferrocene trisulfides that bear

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[1] Zeldin, M.; Wynne, K.; Allcock, H. A. *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988. Mark, J. E.; Allcock, H. A.; West, R. *Inorganic Polymers*; Prentice-Hall: Englewood Cliffs, NJ, 1992.

[2] Daum, P.; Murray, R. W. *J. Phys. Chem.* **1981,** *85,* 389 and references therein.

[3] Brown, G. M.; Meyer, T. J.; Cowan, D. O.; LeVanda, C.; Kaufman, F.; Roling, P. V.; Rausch, M. D. *Inorg. Chem.* **1975,** *14,* 506.

[4] Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992,** *114,* 6246. Foucher, D. A.; Manners, I. *Makromol. Chem., Rapid Commun.* **1993,** *14,* 63. Tang, B.-Z.; Petersen, R.; Foucher, D. A.; Lough, A.; Coombs, N.; Sodhi, R.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1993,** 523.

[5] Angelakos, C.; Zamble, D. B.; Foucher, D. A.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1994,** *33,* 1709 and references therein.

[6] Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971,** *27,* 241. Davison, A.; Smart, J. C. *J. Organomet. Chem.* **1979,** *174,* 321.

[7] Davis, B. R.; Bernal, I. *J. Cryst. Mol. Struct.* **1972,** *2,* 107.

[8] Abel, E. W.; Booth, M.; Orrell, K. G. *J. Organomet. Chem.* **1980,** *186,* C37.

[9] In addition to ref 8 see also: Abel, E. W.; Booth, M.; Orrell, K. O. *J. Organomet. Chem.* **1981,** *208,* 213. Abel, E. W.; Orrell, K. G.; Osborne, A. G.; Sik, V. *J. Organomet. Chem.* **1991,** *411,* 239.

[10] Broussier, R.; Abdulla, A.; Gautheron, B. *J. Organomet. Chem.* **1987,** *332,* 165.

[11] Akabori, S.; Kumagal, T.; Shirahige, T.; Sato, S.; Kawazoe, K.; Tamura, C.; Sato, M. *Organometallics* **1987,** *6,* 526. Akabori, S.; Kumagi, T.; Shirahige, T.; Sato, S.; Kawazoe, K.; Tamura, C.; Sato, M. *Organometallics* **1987,** *6,* 2105. Dilworth, J. R.; Ibrahim, S. K. *Transition Met. Chem.* **1991,** *16,* 239. Seyferth, D.; Hames, B. W.; Rucker, T. G.; Cowie, M.; Dickson, R. S. *J. Organomet. Chem.* **1987,** *326,* 269. Seyferth, D.; Hames. B. W. *Inorg. Chim. Acta* **1983,** *77,* L1.

[12] Nuyken, O.; Pöhlmann, T.; Herberhold, M. *Macromol. Rep.* **1992,** *3,* 211. Herberhold, M.; Brendel, H.-D.; Nuyken, O.; Pöhlmann, T. *J. Organomet. Chem.* **1991,** *413,* 65.

[13] Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992,** *114,* 1926.

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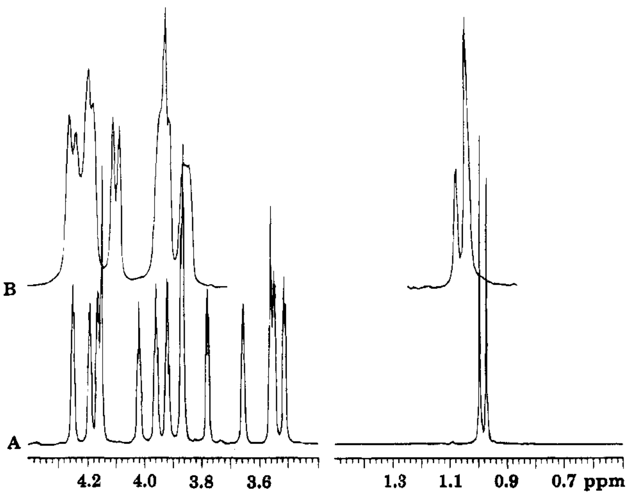


Figure 1. 400 MHz ^1H NMR spectra of C_6D_6 solutions of (A) *t*-BufcS_3 and (B) [*t*-Bu$fcS_2]_n$.

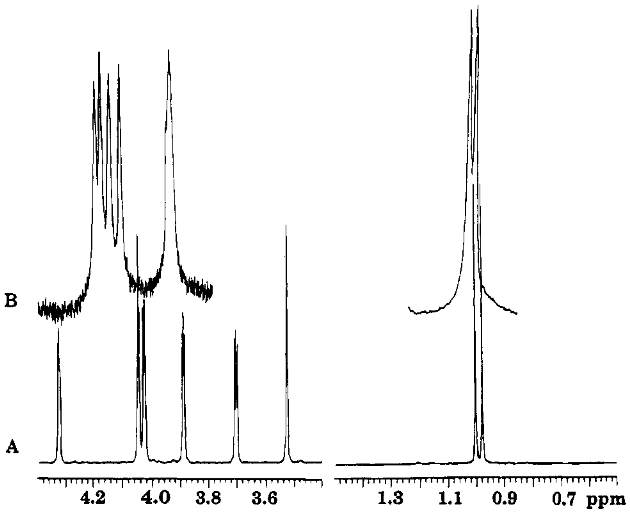


Figure 2. 400 MHz ^1H NMR spectra of C_6D_6 solutions of (A) [(*t*-Bu)$_2fcS_3]_n$ and (B) [(*t*-Bu)$_2fcS_2]_n$.

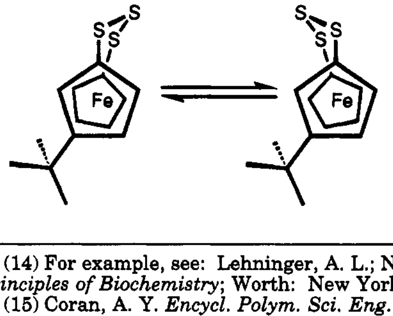
alkyl substituents in a search for soluble polymers. Our initial report focused on polymers derived from a mixture of 1,2,1′- and 1,3,1′-*n*-butylferrocene trisulfide. The present study focuses on developing monomers with stereochemistries simpler than that seen for *n*-BufcS_3.

It is important to recognize that many persulfide-containing polymers are known. Most proteins, of course, feature S—S cross-links based on cystine residues.[14] Similarly, the vulcanization of polyolefins with sulfur introduces oligosulfide cross-links between polyolefin chains.[15] Also relevant are the thiokol polymers prepared by the reaction of alkali-metal polysulfides with alkyl dihalides.[16]

Results

Substituted Ferrocene Trisulfides. The trithiaferrocenophanes discussed in this paper include $(C_5H_4)_2FeS_3$, (*t*-Bu$C_5H_3)(C_5H_4)FeS_3$, and (*t*-Bu$C_5H_3)_2FeS_3$. These species will be referred to as fcS_3, *t*-BufcS_3, and (*t*-Bu)$_2fcS_3$, respectively.

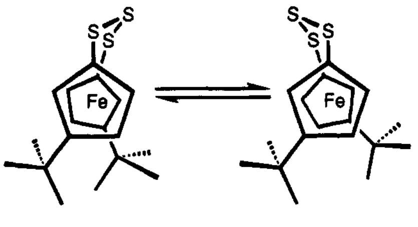
The species *t*-BufcS_3 was obtained in good yield from *t*-Bufc using the lithiation procedure of Smart and Davison. This trisulfide was isolated as an orange oil that slowly solidified. Its formula was confirmed by microanalysis and mass spectrometry. Its ^1H NMR spectrum exhibits 13 multiplets in the region 3.5–4.5 ppm (one with relative intensity 2), corresponding to 14 diastereotopic C_5H_x protons (Figure 1). The *t*-Bu resonances appear as a pair of equally intense singlets near 1.0 ppm. These results indicate that the species exists only as a pair of conformers derived from a single regioisomer (eq 2). Given the steric bulk of the *t*-Bu group, it is reasonable to assume that this isomer corresponds to the 1,3,1′-derivative. The fact that the equilibrium quotient for this conformational equilibrium is nearly unity indicates that the trisulfide unit is distant from the *t*-Bu substituent.



(2)

The preparation of (*t*-Bu)$_2fcS_3$ required the synthesis of 1,1′-di-*tert*-butylferrocene. This in turn entailed the synthesis of *t*-BuC_5H_4M (M = Na, Li, MgX), which we initially attempted to prepare via alkylation of NaC_5H_5 with *t*-BuCl. A more reliable route to *t*-BuC_5H_4Li involves the addition of MeLi to 6,6-dimethylfulvene.[17] *t*-BuC_5H_4Li was isolated from this reaction and identified spectroscopically. Treatment of *t*-BuC_5H_4Li with $FeCl_2$ afforded (*t*-Bu$C_5H_4)_2Fe$ in multigram amounts. Dilithiation of (*t*-Bu)$_2$fc followed by treatment with elemental sulfur afforded (*t*-Bu)$_2fcS_3$ in good yield. This species proved very soluble in nonpolar organic solvents and could be crystallized efficiently from cold hexanes. This highly soluble ferrocene trisulfide tended to be contaminated with elemental sulfur. This impurity obviously does not reveal itself in the ^1H NMR analysis but does so when microanalysis is performed. Since the polymerization protocols require the use of sulfur-abstracting agents, it was especially important to deal with this problem. We found that the extra sulfur could be removed by chromatography of the ferrocene trisulfide on a highly cross-linked polystyrene gel.

The ^1H NMR spectrum of (*t*-Bu)$_2fcS_3$ shows two equally intense *t*-Bu resonances as well as six C*H* signals. On the basis of the aforementioned arguments, we assume that the metalation occurs at the positions β with respect to the *t*-Bu groups (see above). The ^1H NMR data confirmed this assignment (Figure 2). The product is a racemic mixture, each enantiomorph of which is subject to the conformation equilibrium associated with the trisulfide (eq 3). Interestingly, however,



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[14] For example, see: Lehninger, A. L.; Nelson, D. C.; Cox, M. M. *Principles of Biochemistry*; Worth: New York, 1993.

[15] Coran, A. Y. *Encycl. Polym. Sci. Eng.* **1989**, *17*, 666.

[16] Tobolsky, A. V.; Macknight W. J. *Polym. Rev.* **1965**, *13*, 35.

Table 1. Selected Bond Distances (Å) and Angles (deg) for (t-Bu)$_2$fcS$_3$

Fe—C1	2.047(7)	C1—C2	1.42(1)
Fe—C2	2.038(8)	C1—C5	1.42(1)
Fe—C3	2.042(7)	C2—C3	1.43(1)
Fe—C4	2.082(7)	C3—C4	1.41(1)
Fe—C5	2.055(7)	C4—C5	1.43(1)
Fe—C10	2.039(7)	C10—C11	1.42(1)
Fe—C11	2.050(7)	C10—C14	1.41(1)
Fe—C12	2.081(6)	C11—C12	1.42(1)
Fe—C13	2.062(7)	C12—C13	1.41(1)
Fe—C14	2.038(7)	C13—C14	1.427(10)
C1—S2	1.750(8)	C4—C6	1.52(1)
C10—S3	1.764(7)	C12—C15	1.54(1)
S1—S2	2.061(3)	S1—S3	2.044(3)
S2—S1—S3	103.7(1)	C10—S3—S1	102.4(3)
C1—S2—S1	104.2(2)	tilt angle[a]	4.4(4)

[a] The tilt angle is defined as the angle formed by the intersection of the planes of the cyclopentadienyl rings.

this conformational equilibrium for the 1,3,1′,4′-isomer yields an indistinguishable conformer. Inversion of the trisulfide strap for the 1,3,1′,3′-isomer would not generate an indistinguishable isomer; these two isomers would each be characterized by a single t-Bu resonance. Since we have shown that there is minimal interaction between the t-Bu group and a trisulfide strap in the 3-position, we would also expect that the two conformers of the 1,3,1′,3′-isomer would occur in equal amounts; hence, the mixture of isomers might appear spectroscopically similar to that for a single stereoisomer of the 1,3,1′,4′-isomer. The result of this fairly complicated stereochemical situation is that the ^{1}H NMR data do not unambiguously distinguish the 1,3,1′,3′- and 1,3,1′,4′-possibilities.

Solid-State Structure of (t-BuC$_5$H$_3$)$_2$FeS$_3$. The structure of (t-Bu)$_2$fcS$_3$ was definitively established by a single-crystal X-ray diffraction experiment. Selected bond distances and angles are presented in Table 1. The molecule is the 1,3,1′,4′-isomer (Figure 3). The structural parameters associated with (t-Bu)$_2$fcS$_3$ are very similar to those for the parent fcS$_3$,[7] whose bond distances and angles are indicated parenthetically in the following discussion. The molecule consists of two nearly parallel cyclopentadienyl rings that are linked by a trisulfide. The tilt angle between the two cyclopentadienyl rings is 4.44(4)°, suggesting that there is little strain imposed on the cyclopentadienyl rings by the trisulfide strap. The cyclopentadienyl rings are eclipsed. The FeC$_{10}$ core is undistorted; the Fe—C distances span the narrow range of 2.036(7)–2.083(7) Å. The C—C distances within the cyclopentadienyl rings range from 1.41(1) to 1.43(10) Å (1.40–1.45 Å). The trisulfide strap is indeed distant from the t-Bu group, consistent with the spectroscopic measurements, showing that the conformers of t-BufcS$_3$ are equally abundant in solution. The S—S—S angle was found to be 103.7(1)° (103.9(2)°).

Synthesis of Poly(ferrocenylene persulfides). The following sections concern the synthesis and properties of polymers derived from the ferrocene trisulfides. In these studies the product mixtures were often analyzed by gel permeation chromatography (GPC), where the elution rates are calibrated relative to polystyrene standards. We recognize that the hydrodynamic properties of our polymer samples probably differ from those for polystyrene. For this reason the results assume importance only as a measure of the *relative* molecular weights of the samples.

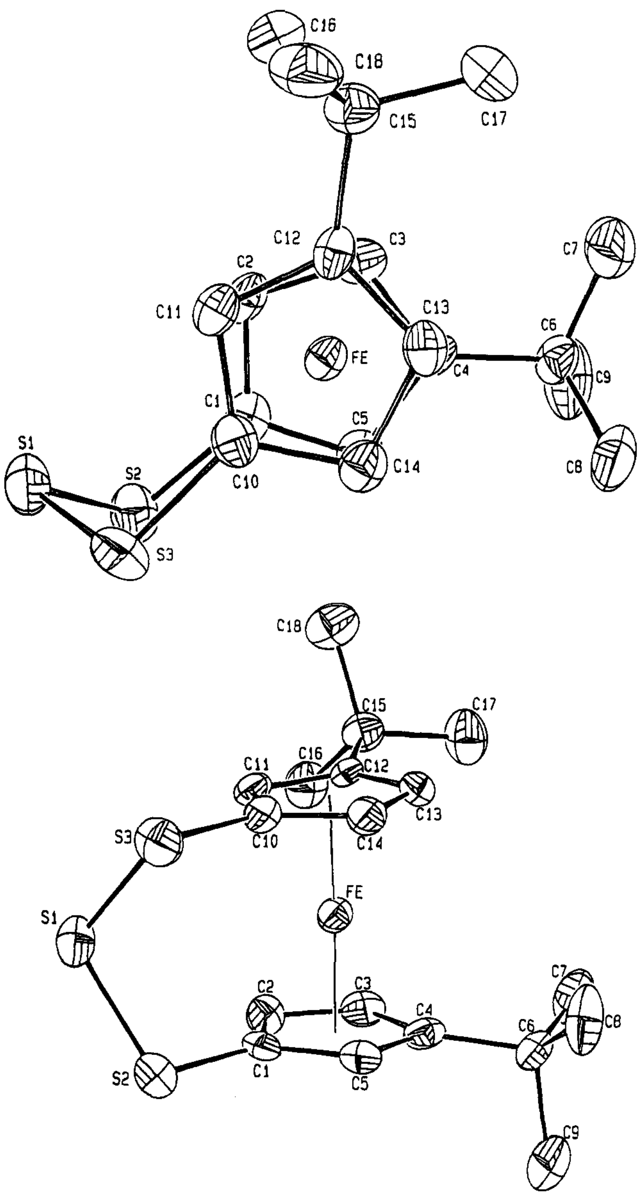

Figure 3. ORTEP drawing of the non-hydrogen atoms in (t-Bu)$_2$fcS$_3$.

Organic solutions of the trisulfides were converted to polymers using 0.95 equiv of Bu$_3$P (eq 4). Bu$_3$P was

$$(\mathrm{RC_5H_3})_2\mathrm{FeS_3} + \mathrm{Bu_3P} \rightarrow [(\mathrm{RC_5H_3})_2\mathrm{FeS_2}]_n + \mathrm{Bu_3PS} \quad (4)$$

added rapidly in one portion to a solution of the trisulfide. The polymerizations are signaled by a darkening of the solution color from yellow to orange. On the basis of the color changes, polymerizations of THF solutions of the trisulfides occur over a period of hours. In contrast, the reactions done in DMF produced the dark orange color after a few seconds. Polymerizations in DMF were also accompanied by the formation of an insoluble dark brown-orange rubbery material whose elemental composition corresponds to the persulfide polymer. After it was dried, this solid was obtained as a brittle glass that swells but does not dissolve in THF.

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(17) Howie, R. A.; McQuillian, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213.

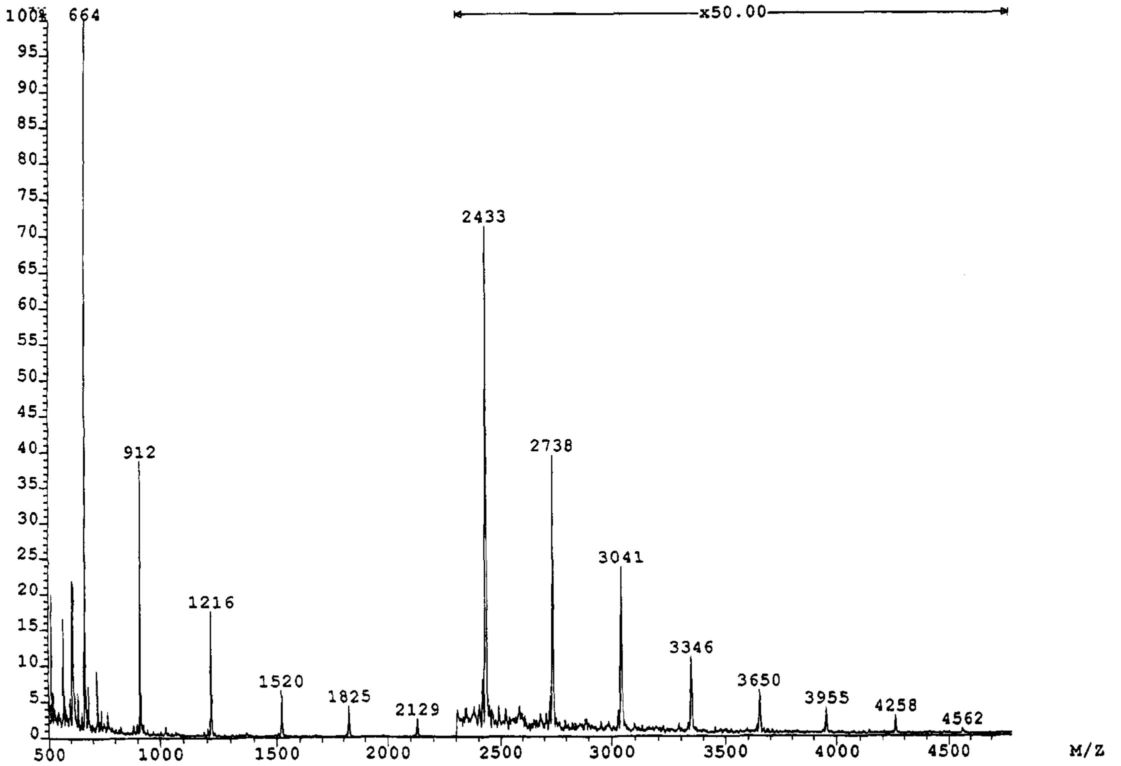

Figure 4. Fast atom bombardment mass spectrum of $[t\text{-BufcS}_2]_n$. Note the change in sensitivity for the high *m/z* range.

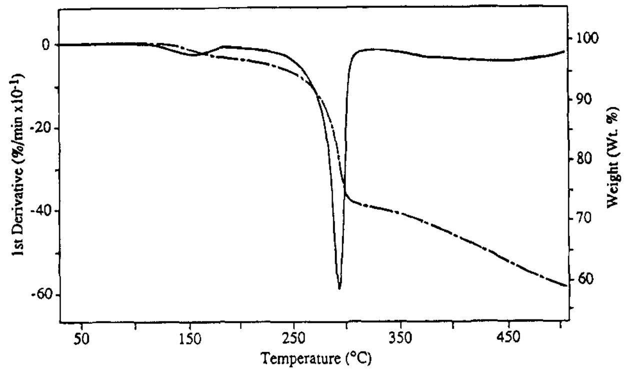

Figure 5. Thermogravimetric analysis of $[t\text{-BufcS}_2]_n$ (heating rate of 10 °C/min, flowing He).

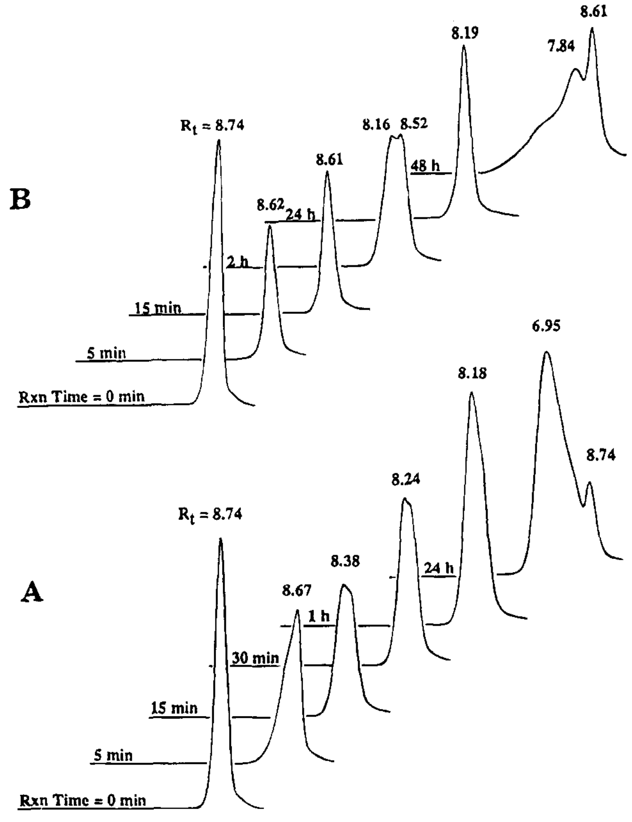

Figure 6. GPC traces for various stages in the desulfurization of (A) $t\text{-BufcS}_3$ and (B) $(t\text{-Bu})_2\text{fcS}_3$ with 0.95 equiv of Bu_3P (mobile phase CH_2Cl_2, elution rate 1.5 mL/min, R_t = retention time).

Desulfurizations of the trisulfides in dichloromethane solutions lead to low-molecular-weight products; this effect remains under study.[18]

The persulfide polymers $[t\text{-BufcS}_2]_n$ and $[(t\text{-Bu})_2\text{fcS}_2]_n$ were obtained as yellow powders after precipitation from THF solutions using methanol. GPC analyses indicated that this reprecipitation procedure removed low-molecular-weight material that included Bu_3PS and unreacted trisulfide. ^{31}P NMR studies on the soluble polymers showed no evidence for residual organophosphorus compounds.

GPC measurements indicated that the *t*-Bu and $(t\text{-Bu})_2$ polymers are polydisperse: M_n = 3700 (M_w = 26 000) and M_n = 2400 (M_w = 19 000), respectively. Fast atom bombardment mass spectroscopy (FABMS) of $[t\text{-BufcS}_2]_n$ showed a progression of peak envelopes ranging from trimer up to the 16mer (Figure 4). Under comparable conditions the mass spectrum of $t\text{-BufcS}_3$ showed no evidence for higher oligomers, hence, the high-*m/z* peaks are not due to the formation of polymers in the mass spectrometer's probe. The strongest peak in the mass spectrum is at *m/z* = 664, which corresponds to $[t\text{-BufcS}_2]_2\text{Fe}$.

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[18] Compton, D. L.; Brandt, P. F.; Rauchfuss, T. B. Unpublished results.

Table 2. Molecular Weights and Polymerization Conditions for $[t\text{-BufcS}_2]_n$ and $[t\text{-Bu}_2\text{fcS}_2]_n$

polymer[a]	solvent	M_w[b]	M_n[b]	M_w/M_n	reacn time
$[t\text{-BufcS}_2]_n$	CH_2Cl_2	3 500	800	4.4	24 h
	THF	26 000	3 700	7.0	72 h
	DMF[c]	23 000	3 500	6.5	10 min
$[(t\text{-Bu})_2\text{fcS}_2]_n$	CH_2Cl_2	1 300	700	1.9	36 h
	THF	19 000	2 400	7.9	96 h
	DMF[c]	14 000	1 900	7.4	15 min

[a] Standard conditions of the polymerizations involved reacting 0.510 mmol of monomer with 0.490 mmol of Bu_3P (0.95 equiv) in 10 mL of solvent. [b] Determined by GPC analysis in CH_2Cl_2 vs polystyrene standards. [c] These polymerizations produced orange insoluble solids.

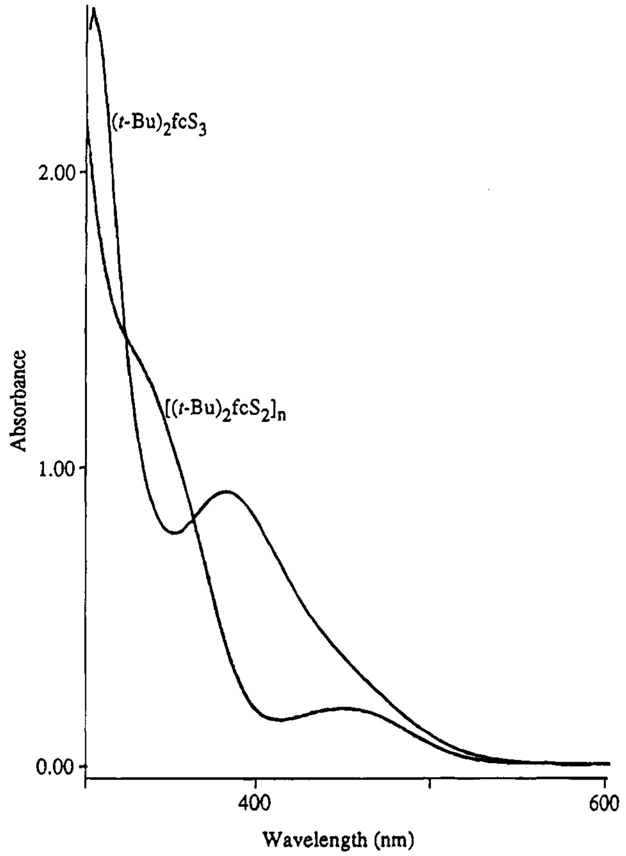


Figure 7. UV–vis spectra of CH_2Cl_2 solutions of $(t\text{-Bu})_2\text{fcS}_3$ and $[(t\text{-Bu})_2\text{fcS}_2]_n$.

The polymers are air stable in the solid state and in solution in the absence of light, as confirmed by ^{1}H NMR and GPC measurements. Thermogravimetric analyses (He atmosphere) showed that the *t*-Bu-substituted polymers are stable up to 260–290 °C (Figure 5). On the basis of the observed weight changes, the polymers appear to decompose via the loss of one or two sulfur atoms. Solutions of the polymers are stable when stored under an inert atmosphere.

In Situ Studies of the Polymerizations. The desulfurization of $t\text{-BufcS}_3$ and $(t\text{-Bu})_2\text{fcS}_3$ with Bu_3P in THF and DMF solution was monitored using GPC. The trisulfide concentration drops concomitant with the growth of a broader peak for higher molecular weight material (Figure 6). In the case of $(t\text{-Bu})_2\text{fcS}_3$ the polymer peak has two maxima. The use of DMF or THF did not greatly affect the molecular weights of the final persulfide polymers (Table 2) although, as mentioned above, the solvent strongly influenced the rates of polymerization. On the basis of the GPC measurements, the conversion of $t\text{-BufcS}_3$ to polymer is approximately twice as fast as for $(t\text{-Bu})_2\text{fcS}_3$.

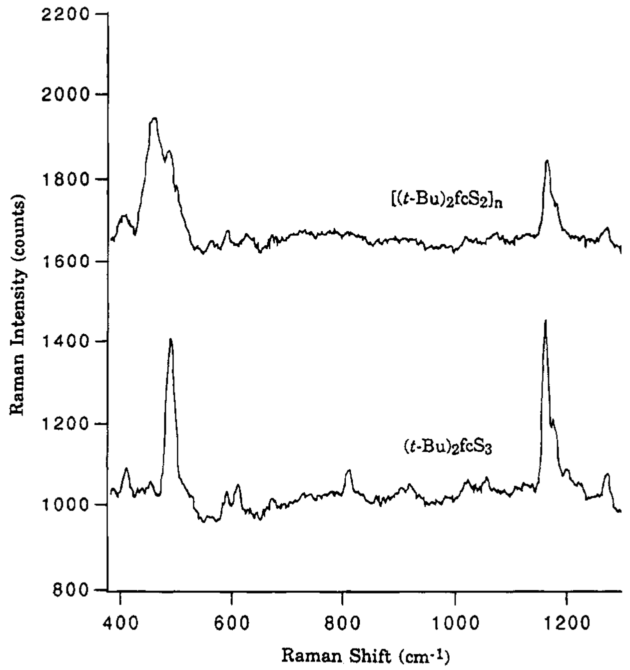


Figure 8. Raman spectra for $(t\text{-Bu})_2\text{fcS}_3$ and $[(t\text{-Bu})_2\text{fcS}_2]_n$ (excitation at 514 nm, 140 mW).

The rates of desulfurization of $t\text{-BufcS}_3$ and $(t\text{-Bu})_2\text{fcS}_3$ were more sensitively evaluated using ^{31}P NMR spectroscopy, by monitoring the conversion of Bu_3P (−29.5 ppm) to Bu_3PS (49.4 ppm). Under otherwise identical conditions, the complete consumption of Bu_3P required 72 and 96 h, for THF solutions of $t\text{-BufcS}_3$ and $(t\text{Bu})_2\text{fcS}_3$, respectively. In contrast, ^{31}P NMR measurements show that conversions of DMF solutions of $t\text{-BufcS}_3$ and $(t\text{-Bu})_2\text{fcS}_3$ are complete after only a few minutes. Even under these conditions of very rapid polymerization, $t\text{-BufcS}_3$ was consumed faster than $(t\text{-Bu})_2\text{fcS}_3$, possibly indicative of a steric influence on the rate of desulfurization (Table 2).

The influence of the Bu_3P:trisulfide ratio was evaluated, again using GPC. For the Bu_3P + $t\text{-BufcS}_3$ reaction in THF, the use of only 0.5 equiv of Bu_3P resulted in low-molecular-weight products ($M_n = 706$, $M_w = 2063$) and only partial conversion of monomer to polymer. When a 2-fold excess of Bu_3P was employed, the trisulfide was completely consumed but we observed only low-molecular-weight oligomers ($M_n = 860$, $M_w = 3300$).

Spectroscopic Properties of the Persulfide Polymers. Solutions of $t\text{-(Bu)}_2\text{fcS}_3$ absorb at 318 and 380 nm, while its polymerized derivative features absorptions at 318 and 448 nm, with an additional shoulder at 320 nm (Figure 7). The shift in the optical properties indicates that the metal center is affected by the change from the trisulfide to the persulfide; this is supported by the electrochemical measurements (see below).

Infrared spectra of the monomers and polymers were generally similar to those of the parent substituted ferrocenes. The ν_{S-S} modes in the polymers were specifically examined, since they were expected to be most sensitive to the polymer structure. The polymers showed only weak IR bands assignable to ν_{S-S} (550–650 cm^{-1}), although their Raman spectra featured intense signals in this region (Figure 8). The Raman

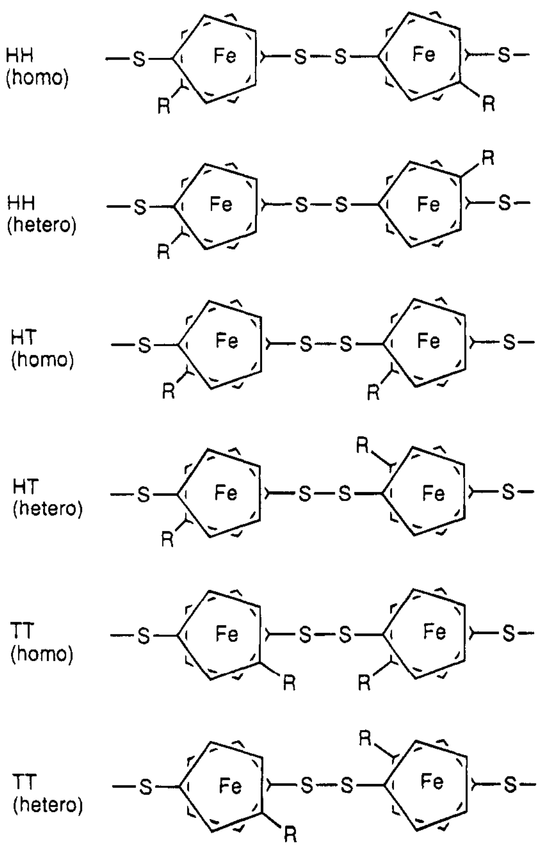


Figure 9. Structures for dyads of [*t*-BufcS$_2$]$_n$, derived from *t*-BufcS$_2$ monomers of the same (homo) or differing (hetero) chiralities.

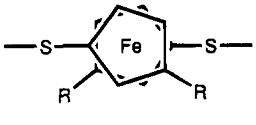
Table 3. Electrochemical Data for Monomers and Polymers

	$^1E_{1/2}{}^{a,b}$ (mV)	$^2E_{1/2}{}^{a,b}$ (mV)	ΔE (V)
t-BufcS$_3$^{c}	803		
(*t*-Bu)$_2$fcS$_3$^{c}	748		
[*t*-BufcS$_2$]$_n$	665	955	0.29
[(*t*-Bu)$_2$fcS$_2$]$_n$	645	935	0.29

[a] $^1E_{1/2}$ and $^2E_{1/2}$ refer to the half-wave potentials for the first and second oxidation waves. [b] The cyclic voltammograms were performed on 1 mmol solutions of the same with 0.1 M of electrolyte ([Bu$_4$N][PF$_6$]) in CH$_2$Cl$_2$. [c] The monomers exhibit only one reversible oxidation; therefore, $^2E_{1/2}$ and ΔE do not apply.

spectrum for [(*t*-Bu)$_2$fcS$_2$]$_n$ shows a broad signal centered at 510 cm^{-1}, while the spectrum for the corresponding trisulfide has one peak at 525 cm^{-1}.

NMR Studies on the Polymers. The stereochemistry of the polymers was probed by ^{1}H NMR spectroscopy. The simpler case is that of [(*t*-Bu)$_2$fcS$_2$]$_n$ because the repeating unit has C_2 symmetry.



The number of stereochemically distinct dyads for this polymer is 2, the homochiral and heterochiral pairs. The ^{1}H NMR spectrum of [(*t*-Bu)$_2$fcS$_2$]$_n$ in the C$_5$*H*$_3$ region consists of five broadened singlets in the ratio 1:1:1:1:2 (Figure 2). Since the two C$_5$H$_3$ groups are equivalent within a given (*t*-Bu)$_2$fcS$_2$ fragment, the multiplicity of the C$_5$*H*$_3$ signals indicates two different sites. Additionally, the spectrum shows two equally intense methyl singlets. This also indicates the presence of two types of (*t*-Bu)$_2$fcS$_2$ sites that, on the basis of integration values, are equally abundant. We conclude that the polymer consists of equal numbers of homochiral and heterochiral dyads.

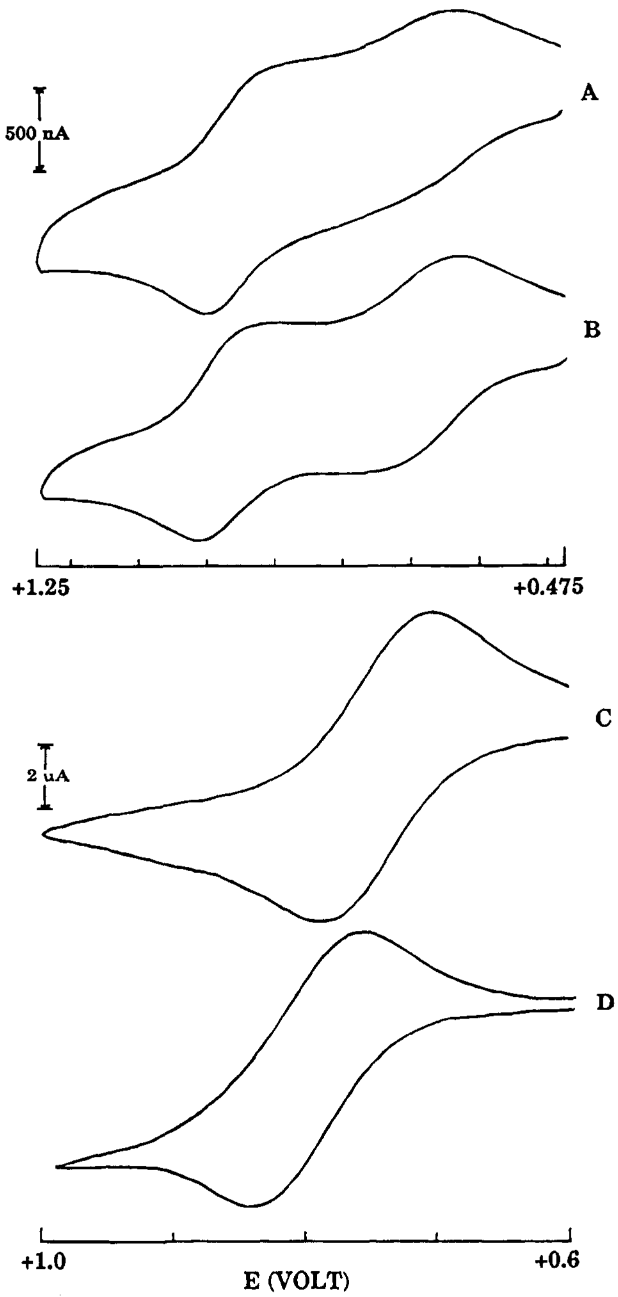


Figure 10. Cyclic voltammograms for 10^{-3} M solutions of (A) [(*t*-Bu)$_2$fcS$_2$]$_n$, (B) [*t*-BufcS$_2$]$_n$, (C) (*t*-Bu)$_2$fcS$_3$, and (D) *t*-BufcS$_3$.

The stereochemical possibilities for [*t*-BufcS$_2$]$_n$ are numerous, since the monomeric fragment is asymmetric. For the sake of discussion we define the head (H) as the *t*-Bu-substituted cyclopentadienyl group.[19] The dyads can be classified according to whether they are head to tail (HT), head to head (HH), or tail to tail (TT). Recognizing that we are working with a racemic mixture, we find that the total number of distinct dyads is 6 (Figure 9). This analysis assumes facile rotation about the S—S bonds. The ^{1}H NMR spectrum of [(*t*-

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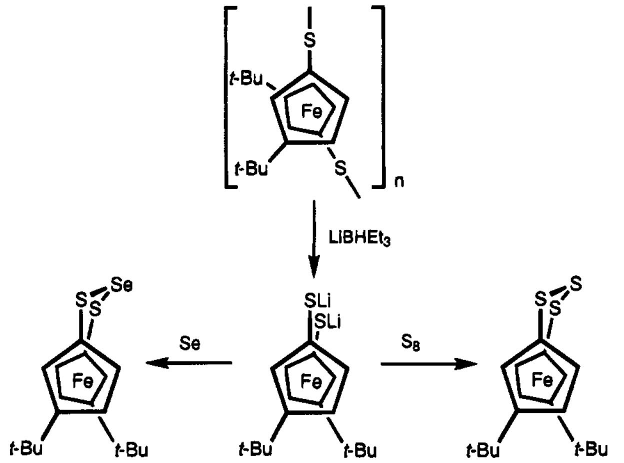
[19] The stereochemical possibilities are analogous to those of polypropylene; see: Farina, M. In *Topics in Stereochemistry*; Eliel, E., Wilen, S. H., Eds.; Wiley: New York, 1987; Chapter 17.

Scheme 1



Bu)fcS$_2$]$_n$ shows four broadened C$_5$$H_x$ peaks. The *t*-Bu signals occur in a 1:2 ratio, although the peak separation is only 0.04 ppm vs 0.11 ppm for the (*t*-Bu)$_2$ polymer. The head to head motif alone gives rise to the interactions proposed for [(*t*-Bu)$_2$fcS$_2$]$_n$. It is likely that this polymer is comprised of a number of different types of dyads.

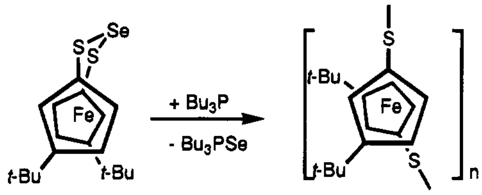
Electrochemistry. The redox properties of the monomers and polymers were evaluated by cyclic voltammetry, the potentials being referenced to Ag/AgCl (Table 3). The neutral trithiaferrocenophanes all undergo one-electron oxidations (Figure 10). These couples are judged to be at least quasi-reversible, since the peak currents for the oxidation and reduction waves are similar. Compared to the parent *t*-Bu-substituted ferrocenes, the trithia derivatives are more difficult to oxidize by ~250 mV. Comparable substituent effects have been observed for other metallocene trichalcogen compounds; e.g., the $E_{1/2}$ value for Fe(C$_5$H$_4$)$_2$S$_3$ is 310 mV more positive than that for ferrocene.[20]

The cyclic voltammograms of the substituted polymers are poorly resolved but clearly feature a pair of quasi-reversible oxidations at ~655 and ~945 mV. The separation between the two waves is ~290 mV. The presence of *two* oxidations indicates that the ferrocenes are relatively strongly coupled. The first oxidation of the polymer occurs at 100–150 mV less than the oxidation of the parent trisulfide. This is interesting, since it indicates that the persulfide group is a relatively better donor than the trisulfide.

Hydride Reduction of [(*t*-Bu)$_2$fcS$_2$]$_n$. The persulfide polymers undergo reductive cleavage with LiBHEt$_3$. Treatment of [(*t*-Bu)$_2$fcS$_2$]$_n$ with 2 equiv of the hydride agent produces (*t*-Bu)$_2$fcS$_2$Li$_2$, which reacts with elemental sulfur to regenerate the parent trisulfide (*t*-Bu)$_2$fcS$_3$. Oxidation of (*t*-Bu)$_2$fcS$_2$Li$_2$ solutions with an excess of iodine gave back [(*t*-Bu)$_2$fcS$_2$]$_n$ (M_w = 16 000, M_n = 2100).

Studies on (*t*-Bu)$_2$fcS$_2$Se. Treatment of (*t*-Bu)$_2$fcS$_2$Li$_2$ solutions with elemental selenium gave (*t*-Bu)$_2$fcS$_2$Se[21] (Scheme 1). The ^{1}H NMR spectrum of this mixed-chalcogen compound exhibits five broad signals (one had doubled intensity) in the region of 3.45–4.5 ppm, integrated for six protons, and a sharp singlet near 1 ppm for the *t*-Bu groups. We attribute the broadened C$_5$$H_3$ signals to the effects of rapid ring inversion for the —S—Se—S— strap. Broadening was not observed for the trisulfide, but this difference was anticipated on the basis of the studies which have shown that the barrier for the inversion of the trichalcogen rings decreased with increasing interchalcogen bond length.[8]

The observation of a single *t*-Bu resonance for (*t*-Bu)$_2$fcS$_2$Se shows that the Se is situated in the central position of the trichalcogen strap. Treatment of THF solutions of (*t*-Bu)$_2$fcS$_2$Se with Bu$_3$P gave [(*t*-Bu)$_2$fcS$_2$]$_n$, identified by its ^{1}H NMR spectrum (eq 5). The ^{31}P NMR spectrum of the reaction mixture showed exclusive formation of Bu$_3$PSe (δ 39.2 ppm), which is readily distinguished from Bu$_3$PS (δ 49.4 ppm). This experiment suggests that the polymerization of the trisulfides is initiated by removal of the *central* sulfur atom.



(5)

Discussion

Poly(ferrocenylene persulfides) are a new family of polymers prepared via the desulfurization of ferrocene trisulfides. The parent [fcS$_2$]$_n$ is insoluble in all solvents with which it does not react. The solubility problem was solved in this work by the use of *tert*-butyl-substituted ferrocenes. Unlike *n*-BufcS$_3$, which was obtained as a mixture of 1,2,1′- and 1,3,1′-isomers, the *t*-Bu-substituted ferrocenes are stereochemically better defined. The corresponding *t*-BufcS$_3$ forms exclusively as the 1,3,1′-isomer. Presumably the lithiation is directed by the steric bulk of the *t*-Bu group, as has been observed previously.[22] More striking is the course of the lithiation of (*t*-BuC$_5$H$_4$)$_2$Fe. Not only do both lithiations proceed with clean 1,3-selectivity but there is also essentially perfect registry between the two cyclopentadienyl rings such that we obtained exclusively the 1,3,1′,4′-isomer. (*t*-Bu)$_2$fcS$_3$ is chiral but converts into a nonidentical but indistinguishable enantiomer upon inversion of the trisulfide strap.

Treatment of the trisulfides with Bu$_3$P gives polymers. ^{1}H NMR measurements suggest that [(*t*-Bu)$_2$fcS$_2$]$_n$ has simpler stereochemistry, as expected, since only two dyads are possible. The molecular weights of the polymers are only modest, especially in comparison with those for [*n*-BufcS$_2$]$_n$ ($M_n \approx 10^5$).[18]

The selection of Bu$_3$P for the polymerizations was based on its high nucleophilicity and the good solubility of its sulfide. These factors lead to both rapid polymerization and easy purification of products. Triorganophosphines are well known to desulfurize oligosulfides

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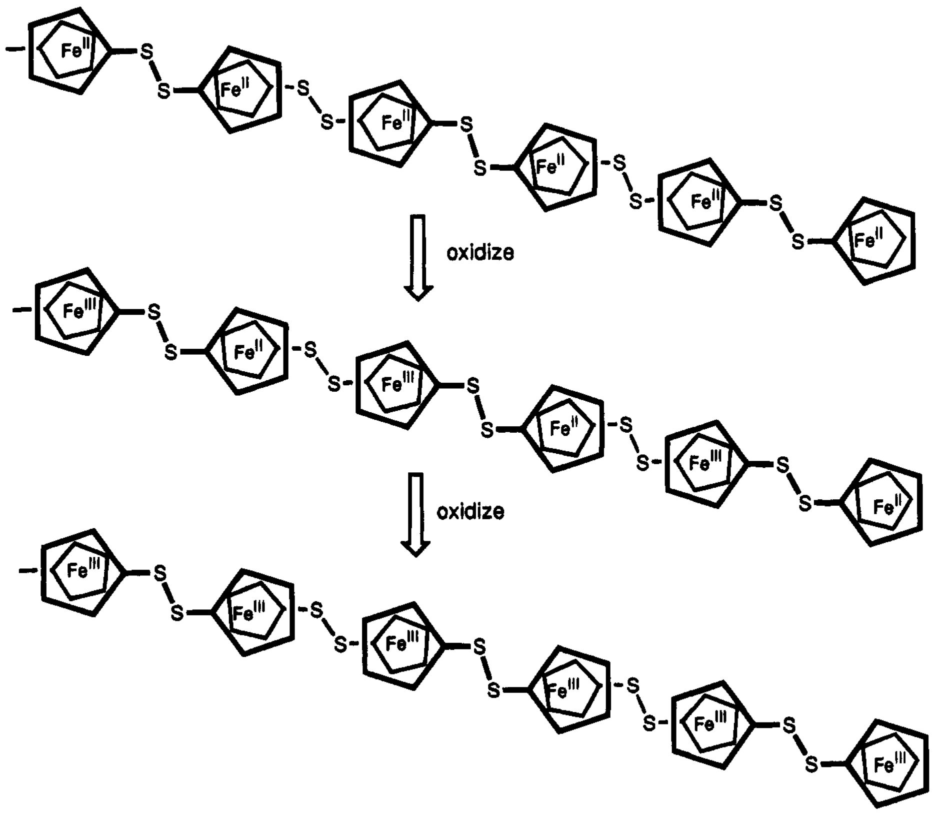
(20) Ushijima, H.; Akiyama, T.; Kajitani, M.; Harada, Y.; Sugimori, A. *Chem. Lett.* **1987**, 2197. Ushijima, H.; Akiyama, T.; Kajitani, M.; Shimizu, K.; Aoyama, M.; Masuda, S.; Harada, Y.; Sugimori, A. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1015. Zanello, P.; Opromolla, G.; Casarin, M.; Herberhold, M.; Leitner, P. *J. Organomet. Chem.* **1993**, *443*, 199.

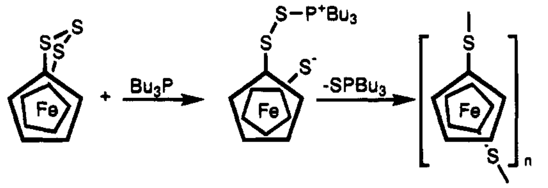
(21) There are many examples of mixed-chalcogen compounds of the type fcE$_2$E′: Osborne, A. G.; Hollands, R. E.; Nagy, A. G. *J. Organomet. Chem.* **1989**, *373*, 229. Osborne, A. G.; Hollands, R. E.; Howard, J. A. K.; Bryan, R. F. *J. Organomet. Chem.* **1981**, *205*, 395. Herberhold, M.; Leitner, P. *J. Organomet. Chem.* **1991**, *411*, 233.

(22) Benkeser, R. A.; Bach, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 890.

Scheme 2

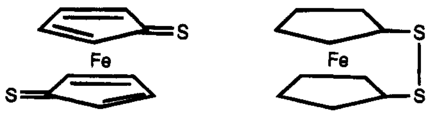


via thiophosphonium intermediates.[23] Polar solvents accelerate the desulfurization of the ferrocene trisulfides, consistent with the involvement of such polar intermediates.[24] Using (t-Bu)$_2$fcS$_2$Se, we demonstrated that it is the central chalcogen that is removed by the phosphine. These observations lead to the mechanism portrayed in eq 6. The steps that occur subsequent to



(6)

the attack by Bu$_3$P are not known. The thiophosphonium salt could eliminate Bu$_3$PS, leading to (C$_5$R$_4$)$_2$FeS$_2$. This species might exist as either the molecular persulfide or the cyclopentadienethione complex.



Complexes of cyclopentadienones are well-known.[25] Structural analogs of the monomeric persulfide are known in the form of the *ansa*-ferrocenes such as (C$_5$H$_4$)$_2$FeSi$_2$Me$_4$[26] and (C$_5$H$_4$)$_2$FeC$_2$Me$_4$.[27] Indeed, (C$_5$H$_4$)$_2$FeC$_2$H$_4$ is demonstrably strained, as it undergoes thermally induced polymerization.[28] For a given series of *ansa*-ferrocenes (C$_5$H$_4$)$_2$FeE$_n$, their kinetic tendency toward polymerization is related to the strain introduced by the bridging group. This is illustrated by Manners' work, which contrasts (C$_5$H$_4$)$_2$FeSiMe$_2$ with the far less reactive (C$_5$H$_4$)$_2$FeSi$_2$Me$_4$.[26] Because sulfur is smaller than silicon ($\Delta r_{\text{cov}} = 0.1$ Å), the strain in (C$_5$H$_4$)$_2$FeS$_2$ can be expected to be greater than that in (C$_5$H$_4$)$_2$FeSi$_2$Me$_4$. Another factor that would facilitate the polymerization of (C$_5$H$_4$)$_2$FeS$_2$ is that S—S bonds have greater reactivity toward nucleophilic cleavage than do Si—Si bonds.

The new polymers can undergo redox conversions at both the iron and S—S centers. Hydride agents attack the S—S bonds, resulting in cleavage of the polymer into dithiolates, which can be reoxidized to give persulfides. The polymers can be oxidized at the iron centers in two steps. The electrochemical data indicate that the first oxidation process occurs on alternating Fe centers, while the second more energetic oxidation converts the polymer to the all-Fe$^{\text{III}}$ derivative (Scheme 2).[29] The degree of interaction between the Fe centers was indicated by the separation of the two redox events. The ΔE values (i.e. ${}^2E_{1/2} - {}^1E_{1/2}$) of [$t$-BufcS$_2$]$_n$ and [(t-Bu)$_2$fcS$_2$]$_n$ are both 290 mV, less than the $\Delta E_{1/2}$ of biferrocene (330 mV),[30] where the metallocenes are directly linked. It is interesting that the persulfide is as effective in promoting electronic coupling as a single SiR$_2$ bridge.[31] It is clear

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(23) Harpp, D. N.; Ash, D. K.; Smith, R. A. *J. Org. Chem.* **1980**, *45*, 5155.

(24) Harpp, D. N.; Smith, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 6046.

(25) Recent work: Kirchner, K.; Mereiter, K.; Schmid, R. *J. Chem. Soc., Chem. Commun.* **1994**, 161. Kirchner, K.; Kwan, K. S.; Taube, H. *Inorg. Chem.* **1993**, *32*, 4974. Kirchner, K.; Taube, H.; Scott, B.; Willett, R. D. *Inorg. Chem.* **1993**, *32*, 1430.

(26) Finckh, W.; Tang. B.-Z.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A.; Manners, I. *Organometallics* **1993**, *12*, 823.

(27) Laing, M. B.; Trueblood, K. N. *Acta Crystallogr.* **1965**, *19*, 373.

(28) Nelson, J. M.; Rengel, H.; Manners, I. *J. Am. Chem. Soc.* **1993**, *115*, 7035.

(29) Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 797.

(30) Dement'ev, V. V.; Cervantes-Lee, F.; Parkanyi, L.; Sharma, H.; Pannell, K. H. *Organometallics* **1993**, *12*, 1983.

from the published record that the coupling between the ferrocene subunits is sensitive to the identity of the intervening bridging atom since R$_2$Ge- and RP-bridged ferrocenes are characterized by $\Delta E_{1/2} \approx 100$ mV.[32] We suggest that the effectiveness of persulfides in promoting electronic coupling between Fe subunits is related to the enhanced ability of persulfides to engage in p−π bonding.[33]

Experimental Section

General Considerations. Preparations employed standard Schlenk tube techniques. Tetramethylethylenediamine (TMEDA) was distilled from Na. Bu$_3$P was purified by vacuum distillation at 0.1 Torr and 110 °C.

Column chromatography was performed on silica gel G (Merck), 0.04−0.063 mm (230−400 mesh). ^{1}H and ^{31}P NMR spectra were recorded on a Varian U-400 spectrometer unless otherwise stated. GPC traces were recorded using a Varian 2510 HPLC pump, TSK guard column, GM H6 column (7.5 mm i.d. × 30 cm), and a Varian 2550 variable wavelength detector eluting at 1.5 mL/min with a detector wavelength of 300 nm. Infrared spectra were recorded on KBr for solids and NaCl plates for liquids using a Mattson Galaxy Series FTIR 3000. UV−vis spectra were recorded using a Hewlett-Packard 8452A spectrophotometer. Elemental analyses were performed by the University of Illinois School of Chemical Sciences microanalytical laboratory.

1,3,1′-*t*-BufcS$_3$. A solution of 10.02 g of *t*-Bufc (41 mmol) in 150 mL of hexane was treated with 51.8 mL of a 1.6 M solution of BuLi (82 mmol) in hexane followed by 12.5 mL of TMEDA (82 mmol). After 20 h, 8.0 g of S$_8$ (250 mmol) was added to the dark red solution; the addition was done in portions over the course of 15 min to avoid effervescence. The red slurry was refluxed for 12 h. The dark red-brown slurry was filtered through a bed of silica gel, which was rinsed with three 100-mL portions of hexanes. The orange filtrate was concentrated to 100 mL *in vacuo*, washed with three 50 mL portions of 10% aqueous NaOH, and dried over Na$_2$SO$_4$. The solvent was removed to give a red oil. Residual *t*-Bufc was removed by distillation at 70 °C (0.05 mm), and excess S$_8$ was removed by elution of a concentrated THF solution through a 30 × 3 cm column of Bio-Beads SX-8, with THF as eluent. The first three-fourths of the broad orange band was collected and evaporated. The resulting red oil was dissolved in a minimal amount (~25 mL) of hot hexanes. Cooling to −20 °C gave an orange solid which was filtered off and dried *in vacuo*. Yield: 8.0 g (58%). Anal. Calcd for $C_{14}H_{16}FeS_3$: C, 50.00; H, 4.80; S, 28.60; Fe, 16.61. Found: C, 49.88; H, 4.80; S, 28.42; Fe, 16.54. ^{1}H NMR (C_6D_6): δ 4.24 (m, 1 H), 4.18 (m, 1 H), 4.15 (m, 2 H), 4.01 (m, 1 H), 3.94 (m, 1 H), 3.90 (m, 1 H) 3.85 (m, 2 H), 3.76 (m, 1 H), 3.65 (m, 1 H), 3.56 (m, 1 H), 3.54 (m, 1 H), 3.50 (m, 1 H), 0.98 (s, 9 H), 0.96 (s, 9 H). UV-vis (CH_2Cl_2): 220, 280, 360 nm. EI MS (70 eV): *m/z* 336 (M$^+$).

6,6-Dimethylfulvene. The synthesis was adapted from that of Freiesleben,[34] and the purification was adapted from that of Thiele.[35] A 250 mL Schlenk flask was charged with 75 mL of acetone (1 mol) followed by 82 mL of freshly cracked cyclopentadiene (1 mol), and the solution was cooled to 0 °C. To this solution was added 7 mL of a 40 wt % solution of MeNH$_2$ catalyst. The reaction solution was warmed to ambient temperature over 2 h with stirring. After 6 h, the yellowish organic layer was removed via cannula, dried over Na$_2$SO$_4$, and purified by distillation (33−37 °C, 5 Torr). The product was stored at −20 °C. Yield: 56 g (53%). ^{1}H NMR (C_6D_6): δ 6.55 (s, 4 H), 1.75 (s, 6 H).

***t*-BuC$_5$H$_4$Li.** This procedure was adapted from that of Howie.[36] A 500-mL Schlenk flask was charged with 29.2 g of 6,6-dimethylfulvene (0.28 mol) followed by 250 mL of Et$_2$O. The solution was cooled to 0 °C, and 196 mL of a 1.4 M solution of MeLi (0.28 mol) in ether was added dropwise. After 2.5 h, the slurry was warmed to ambient temperature and filtered to give a pale yellow powder. This material was dissolved in 150 mL of THF and reprecipitated with 300 mL of hexanes. The white solid was washed with several portions of hexanes. Yield: 33.7 g (94%). Anal. Calcd for $C_9H_{13}Li$: C, 84.36; H, 10.23; Li, 5.41. Found: C, 84.11; H, 10.20; Li, 5.24. ^{1}H NMR (THF-d_8): δ 5.49, 5.12 (pseudo d of t, 4 H), 1.21 (s, 9 H).

1,1′-(*t*-Bu)$_2$fc. A 500 mL Schlenk flask was charged with 4.95 g of FeCl$_2$ (39.0 mmol) and 10.0 g of *t*-BuC$_5$H$_4$Li (78 mmol). The flask was cooled to 0 °C, and 250 mL of THF was added slowly over 20 min; the resulting red solution was refluxed for 12 h. The reaction vessel was cautiously opened to the air, and the mixture was diluted with 500 mL of hexanes and filtered through silica gel, which was further washed with 200 mL of hexanes. Evaporation of the solvent gave 9.9 g of a red oil (85%). Anal. Calcd for $C_{18}H_{26}Fe$: C, 72.49; H, 8.79. Found: C, 72.52; H, 8.81. ^{1}H NMR (C_6D_6): δ 4.01, 3.82 (pseudo d of t, 8 H), 1.21 (s, 18 H).

1,3,1′,4′-(*t*-Bu)$_2$fcS$_3$. A 250 mL flask was charged with 10.01 g of (*t*-Bu)$_2$fc (34 mmol), 200 mL of hexanes, 42.5 mL of a 1.6 M solution of BuLi (68 mmol) in hexane, and 10.3 mL of TMEDA (68 mmol). After 24 h, 10.0 g of S$_8$ (312 mmol) was added in four equal portions over 15 min. The dark red slurry was refluxed for 24 h, resulting in a dark red-brown slurry, which was filtered through a silica gel bed followed by washing with 300 mL of hexanes. The orange filtrate was washed with 10% aqueous NaOH solution, and the organic phase was dried over Na$_2$SO$_4$. Excess S$_8$ was removed by chromatography on a 30.0 × 3.0 cm column of Bio-Beads SX-8, with THF as eluent, by collecting the first three-fourths of the broad orange band. The solvent was removed, and the orange solid was dissolved in a minimal amount of hot hexanes followed by cooling to −20 °C to give orange microcrystals. Yield: 3.5 g (26%). Anal. Calcd for $C_{18}H_{24}FeS_3$: C, 55.09; H, 6.17; S, 24.51; Fe, 14.23. Found: C, 54.99; H, 6.13; S, 24.51; Fe, 14.23. ^{1}H NMR (C_6D_6): δ 4.32 (m, 1 H), 4.05 (m, 1 H), 4.03 (m, 1 H), 3.89 (m, 1 H), 3.70 (m, 1 H), 3.53 (m, 1 H), 1.00 (s, 9 H), 0.98 (s, 9 H). UV−vis (CH_2Cl_2): 314, 380 nm. EI MS (70 eV): *m/z* 392 (M$^+$).

(*t*-Bu)$_2$fcS$_2$Se. A 25 mL flask was charged with a solution of 0.11 g of [(*t*-Bu)$_2$fcS$_2$]$_n$ (0.31 mmol) in 5 mL of THF followed by 0.62 mL of 1 M LiBHEt$_3$ in THF (0.62 mmol). The orange solution was stirred for 0.5 h and then added dropwise to a slurry of 0.97 g of red selenium (1.14 mmol) in 10 mL of THF cooled to 0 °C. The red reaction mixture was warmed to ambient temperature. After a further 3 h, the reaction mixture was quenched with 3 drops of degassed concentrated HCl. After a further 1 h the reaction mixture was treated with 25 mL of water and the washings were extracted twice with 10 mL of hexanes. The combined organic layers were dried over Na$_2$SO$_4$, and the solvents were evaporated. The resulting red oil was purified by column chromatography on silica gel with hexanes as eluent. The first broad orange band was evaporated to give 0.71 g of a red-orange solid (53%). Anal. Calcd for $C_{18}H_{24}FeS_2Se$: C, 49.21; H, 5.51. Found: C, 50.14; H, 5.64. ^{1}H NMR (200 MHz, C_6D_6): δ3.47 (b s, 1 H), 4.05 (b s, 2 H), 3.88 (b s, 1 H), 3.72 (b s, 1 H), 3.48 (b s, 1 H), 1.01 (s, 18 H).

Deselenization of (*t*-Bu)$_2$fcS$_2$Se. A 25 mL Schlenk flask was charged with a solution of 0.50 g of (*t*-Bu)$_2$fcS$_2$Se (1.14 mmol) in 5 mL of THF. The orange-red solution was treated

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(31) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Pannell, K. H. *Chem. Mater.* **1993**, *5*, 1389.

(32) Foucher, D. A.; Honeyman, C. H.; Nelson, J. M.; Tang, B. Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1709 and references therein.

(33) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1987**, *26*, 3328 and references therein.

(34) Freiesleben, W. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 396; *Angew. Chem.* **1963**, *75*, 576.

(35) Thiele, J. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 666.

(36) Howie, R. A.; McQuillian, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213.

with 0.27 mL of Bu_3P (1.08 mmol) and was protected from light. After 72 h, 50 mL of MeOH was added to the dark orange solution. The yellow precipitate was collected by filtration onto a bed of Celite, which was washed twice with 30 mL of MeOH. The yellow solid was extracted from the Celite with 60 mL of THF, and the extract was concentrated to 20 mL. The product was reprecipitated with 50 mL of MeOH. The yellow solid was again collected by filtration through a Celite bed followed by extraction of the yellow solid from the Celite with THF as described above. Slow evaporation of this solution gave an orange glassy film of $[(t\text{-Bu})_2fcS_2]_n$. Yield: 0.24 g (62% based on Bu_3P). ^1H NMR and elemental analysis correspond to those obtained for $[(t\text{-Bu})_2fcS_2]_n$ synthesized from the desulfurization of $(t\text{-Bu})_2fcS_3$.

$[t\text{-BufcS}_2]_n$. A solution of 0.512 g of t-BufcS$_3$ (1.52 mmol) in 20 mL of THF was treated with 0.36 mL of Bu_3P (1.44 mmol), resulting in an orange solution. The reaction mixture was protected from the light. After 72 h, 50 mL of MeOH was added to the now dark orange solution. The yellow precipitate was collected by filtration onto a bed of Celite, which was washed twice with 30 mL of MeOH. The precipitate was extracted from the Celite with 60 mL of THF, and the extract was concentrated to 20 mL. The product was reprecipitated with 50 mL of MeOH. The yellow solid was again collected by filtration through a Celite bed followed by extraction of the yellow solid from the Celite with THF as described above. Slow evaporation of this solution gave an orange glassy film. Yield: 0.39 g (89% based on Bu_3P). Anal. Calcd for $C_{14}H_{16}FeS_2$: C, 55.27; H, 5.30; Fe, 18.36; S, 21.08. Found: C, 54.74; H, 5.64; Fe, 17.92; S, 20.32. ^1H NMR (C_6D_6): δ 4.26, 4.24, 4.20, 4.18, 4.11, 4.09, 3.94, 3.93, 3.91, 3.85 (b s, 14 H), 1.04, 1.00 (b s, 18 H). UV–vis (CH_2Cl_2): 280, 320 (sh), 360 nm. The FAB mass spectrum of this polymer is presented in Figure 4. A high-resolution measurement of the m/z 664 peak gave the value 663.945 30, which can be compared with several matches, including 663.945 00 ($C_{30}H_{24}FeO_2S_6$), 663.9442 53 ($C_{29}H_{28}Fe_2OS_5$), and 663.943 506 ($C_{28}H_{32}Fe_3S_4$).

The same procedure was followed as stated above, except the polymerization was carried out in 20 mL of DMF for 24 h. In addition to 0.15 g of the same product as above (34% yield), a rubbery orange product was obtained. Yield: 0.21 g (47%). Anal. Calcd for $C_{14}H_{16}FeS_2$ (for the insoluble rubber): C, 55.27; H, 5.30; Fe, 18.36; S, 21.08. Found: C, 54.52; H, 5.59; Fe, 18.04; S, 20.23.

The same polymerization in THF was followed as above, except only 0.50 equiv of Bu_3P was used. The reaction mixture was stirred for 72 h and remained yellow. The yellow precipitate was collected by filtration onto a bed of Celite, which was washed twice with 30 mL of MeOH. The precipitate was extracted from the Celite with 60 mL of THF, and the extract was concentrated to 20 mL. The product was reprecipitated with 50 mL of MeOH. The yellow solid was again collected by filtration onto Celite and extracted into THF as described above. Slow evaporation of this solution gave a yellow solid. Yield: 0.39 g (89%, based on Bu_3P). Anal. Calcd for $C_{14}H_{16}FeS_2$: C, 55.27; H, 5.30; Fe, 18.36; S, 21.08. Found: C, 54.87; H, 5.45; Fe, 18.02; S, 20.67.

$[(t\text{-Bu})_2fcS_2]_n$. A solution of 0.201 g of $(t\text{-Bu})_2fcS_3$ (0.512 mmol) in 10 mL of THF was treated with 0.12 mL of Bu_3P (0.49 mmol). After 72 h, 25 mL of MeOH was added to the now dark orange solution. The yellow precipitate was filtered onto a pad of Celite, which was washed twice with 30 mL of MeOH. The filtrate was discarded, and the product was extracted from the Celite with three 20 mL portions of THF. The THF filtrate was concentrated to 10 mL, and the product was reprecipitated with 25 mL of MeOH. The solid was again isolated by filtration onto Celite followed by extraction of the Celite with THF as described above. Slow evaporation of the solvent *in vacuo* gave 0.083 g (47% based on Bu_3P) of an orange film. Anal. Calcd for $C_{18}H_{24}FeS_2$: C, 60.00; H, 6.71; Fe, 15.50; S, 17.79. Found: C, 59.17; H, 7.56; Fe, 14.91; S, 16.83. ^1H NMR (C_6D_6): δ 4.23 (br s, 1 H), 4.21 (br s, 1 H), 4.17 (br s, 1 H), 4.12 (br s, 1 H), 3.88 (br s, 2 H), 1.21 (br s, 9 H), 1.10 (br s, 9 H). UV–vis (CH_2Cl_2): 318, 338 (sh), 449 nm.

Table 4. Atomic Coordinates for the Crystal Structure of $[(t\text{-Bu})_2fcS_2]_n$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Fe	0.2464(1)	0.0333(6)	0.8090(8)
S1	0.1484(2)	0.2159(1)	0.9849(2)
S2	−0.0166(2)	0.1462(1)	0.9220(2)
S3	0.2668(2)	0.1192(2)	1.0553(2)
C1	0.0528(7)	0.0859(5)	0.8183(6)
C2	0.1189(7)	0.1175(5)	0.7274(6)
C3	0.1504(7)	0.0413(6)	0.6652(6)
C4	0.1054(7)	−0.0367(5)	0.7152(6)
C5	0.0453(7)	−0.0085(5)	0.8111(6)
C6	0.0974(8)	−0.1313(5)	0.6724(6)
C7	0.1998(7)	−0.1432(4)	0.5863(5)
C8	0.1248(7)	−0.1991(4)	0.7584(5)
C9	−0.0477(10)	−0.1436(5)	0.6265(5)
C10	0.3428(7)	0.0668(5)	0.9472(6)
C11	0.4083(7)	0.1095(5)	0.8869(6)
C12	0.4589(6)	0.0421(5)	0.7958(6)
C13	0.4215(7)	−0.04113(5)	0.8374(6)
C14	0.3487(7)	−0.0263(5)	0.9316(6)
C15	0.5521(8)	0.0615(5)	0.7029(6)
C16	0.4954(8)	0.1369(5)	0.6338(6)
C17	0.5706(9)	−0.0225(5)	0.6369(7)
C18	0.6930(8)	0.0896(6)	0.7497(6)

The same procedure was followed as stated above, except the polymerization was carried out in 20 mL of DMF for 24 h. In addition to the soluble polymer (0.041 g, 23% yield), we also obtained 0.12 g of an insoluble orange solid (yield 68%). Anal. Calcd for $C_{18}H_{24}FeS_2$ (the insoluble fraction): C, 60.00; H, 6.71; Fe, 15.50; S, 17.79. Found: C, 59.34; H, 6.89; Fe, 15.06; S, 17.13.

X-ray Structural Analysis of $(t\text{-Bu})_2fcS_3$. Crystals were grown by cooling a hexane solution to −4 °C. A transparent orange plate of dimensions 0.1 × 0.2 × 0.5 mm was mounted on a glass fiber. The crystals are monoclinic, space group $P2_1/a$, with a = 9.725(4) Å, b= 14.979(6) Å, c = 12.745(5) Å, α and γ = 90°, β = 91.38(1)°, Z = 4, and d_{calcd} = 1.040 g/cm^3. The iron and sulfur atoms were obtained by direct methods. The remaining atoms were located by cycles of least-squares refinement and difference Fourier maps using the SHELXS-76 programs. Hydrogen atom positions were calculated, and these atoms were included in structure factor calculations and refined with common isotropic thermal parameters. The data were refined to R = 0.0476 and R_w = 0.0485. Atomic coordinates for non-hydrogen atoms are given in Table 4.

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Supplementary Material Available: For the crystallographic determination of $(t\text{-Bu})_2fcS_3$, tables of crystal and data collection details, atomic coordinates, thermal parameters, and all bond distances and angles (11 pages). Ordering information is given on any current masthead page.

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