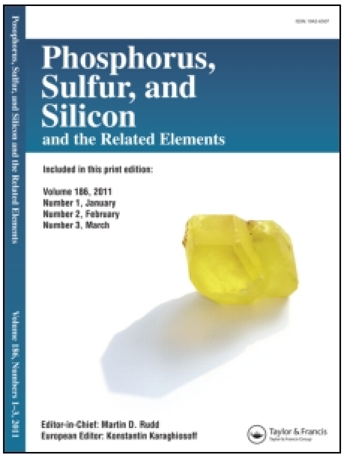

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Thomas B. Rauchfuss[a]; Collin P. Galloway[a]
[a] School of Chemical Sciences and the Materials Research Laboratory, University of Illinois, Urbana, IL, USA

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SYNTHESIS OF INORGANIC AND ORGANOMETALLIC POLYMERS BY DESULFURIZATION OF POLYSULFIDO COMPOUNDS

THOMAS B. RAUCHFUSS AND COLLIN P. GALLOWAY
School of Chemical Sciences and the Materials Research
Laboratory, University of Illinois, Urbana, IL 61801, USA

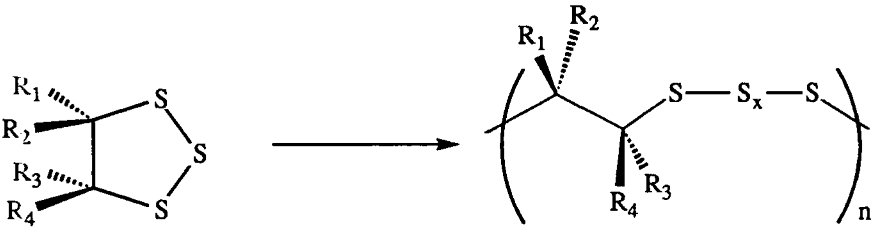
Abstract The paper summarizes background and recent developments in the preparation of organometallic and inorganic polymers from polysulfide precursors.

INTRODUCTION

One of the best known phenomena in main group chemistry is the reversible polymerization of S_8. This time honored reaction suggests the feasibility of preparing stable polymers comprised at least in part of S_x linkages. This view is reinforced by the fact that polysulfide-containing polymers are of major significance as they encompass sulfur-vulcanized polyolefins and cystine-containing proteins. Nonetheless polymers consisting of polysulfide repeat units are not widely recognized although some are items of commerce.

An important class of polysulfide polymers can be prepared via treatment of polysulfide anions with organic dihalides. The resulting so called Thiokol LP polysulfide polymers are of interest for their resistance to permeation by gases, fuels, and solvents.[1] Commercial applications of the LP polymers are found in the insulating glass industry.[2]

Polysulfide polymers have also been prepared by the ring opening reactions of strained trithiacyclopentanes via both anionic and thermal initiation. Tetrafluoro-1,2,3-trithia-cyclopentane forms a brittle white polymer in the presence of weak bases, such as acetonitrile, ethanol, or acetone, but the highest molecular weights were obtained at -80 °C with $P(OMe)_3$ as the initiator.[3] Norbornene trisulfide undergoes anionic polymerization in the presence of sodium phenoxide to give polymers with M_n up to 10^5.[4] High molecular weight polymers were obtained from the thermal polymerization of 4-ethyl-1,2,3-trithiacyclopentane.[5] Radical formation via homolytic S-S bond scission has been invoked as the most probable polymerization pathway for this compound. Likewise, radical polymerization of dicyclopentadienetrisulfide apparently occurs above 170 °C.[6] Compositionally, these polymers have an average of three sulfur atoms per repeat unit, however they may have 2, 3, or 4 contiguous sulfur atoms in the chain (eq. 1).

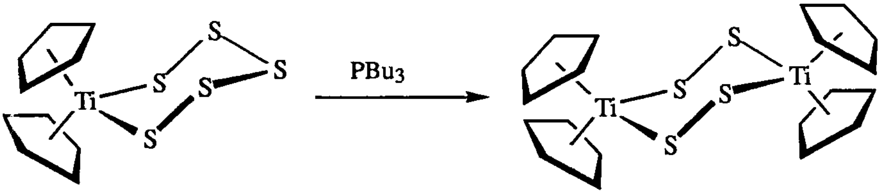


(1)

It is interesting to consider extending the aforementioned methods to the preparation of polysulfide polymers containing transition metals. A very simple approach might entail treatment of a transition metal dihalide with polysulfide salts, analogous to the preparation of Thiokol polymers. Alternatively one could attempt ring-opening polymerization of cyclic transition metal polysulfides. This report summarizes our efforts along these lines. Coincident with our studies on the condensation of metal polysulfides, the number of polysulfido, polyselenido, and polytellurido has grown considerably. Thus the situation is very encouraging: new methods of polymerization are being developed at the same time as new polymerizable substrates are being synthesized.

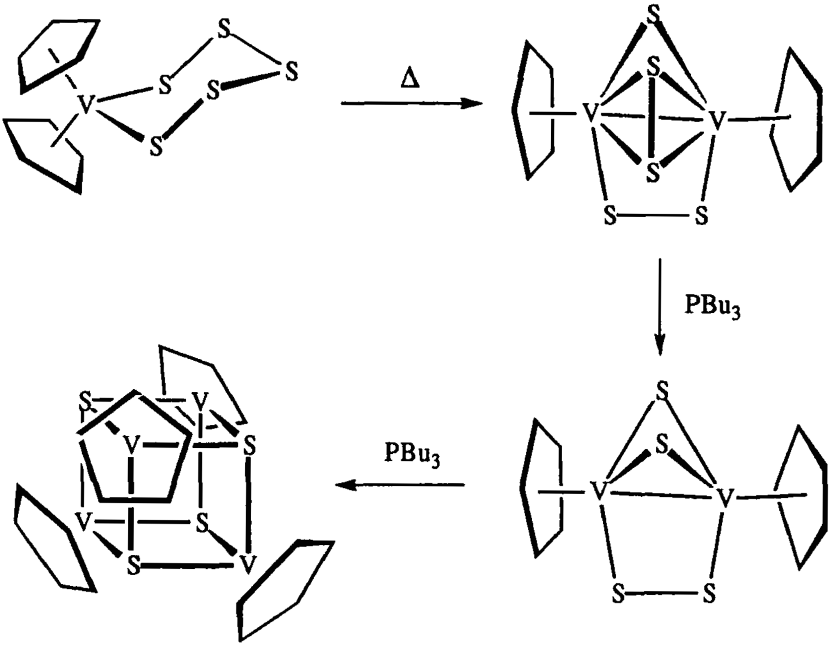
PART I. BACKGROUND STUDIES AND CONCEPTS

Early work from our group showed that metal polysulfido complexes oligomerize upon desulfurization. For example treatment of $(C_5H_5)_2TiS_5$ with tributylphosphine gives $(C_5H_5)_4Ti_2S_4$.[7] With the less aggressive desulfurization agent PPh_3, one obtains $(C_5H_5)_4Ti_2S_6$. These reactions involve attack of the phosphine on the polysulfide ligand with the formation of a desulfurized organometallic intermediate $(RC_5H_4)_2TiS_{5-x}$ which undergoes subsequent dimerization. The success of the method hinges on the fact that the sulfur abstracting group does not bond to the metal and that even upon ring contractions, the shortened oligosulfide remains ligated (eq. 2).



(2)

Concurrent with our work on titanium polysulfides we examined analogous vanadium compounds. At that time it was known that $(C_5H_5)_2VS_5$ is thermally unstable with respect to the then ill defined species $[(C_5H_5)_2V_2S_5]_n$. We prepared the more soluble methylcyclopentadienyl analogs and demonstrated that $(MeC_5H_4)_2V_2S_5$ is molecular.[8] It adopts an interesting structure featuring three types of sulfur ligands. Monodesulfurization of such species generates $(RC_5H_4)_2V_2S_4$, which is susceptible to further desulfurization to give a mixture of the clusters $(RC_5H_4)_4V_4S_4$ and $(RC_5H_4)_5V_5S_6$ (Scheme 1, the V_5S_6 cluster is not shown).[9]



SCHEME 1

This result demonstrated for the first time that desulfurization could lead to clusters, the obvious requirement being that the spectator ligands, in this case RC_5H_4, allow the reactive metal fragment to do more than just cyclize. This was not the case in the Ti chemistry since the *pair* of RC_5H_4 ligands sterically limits the oligomerization pathways for the transient $(RC_5H_4)_2TiS_{5-x}$. The studies on monocyclopentadienyl complexes were extended to ruthenium where desulfurization of $(C_5Me_5)_2Ru_2S_4$ led to $(C_5Me_5)_4Ru_4S_6$. In this case we could demonstrate the formation of the transient $(C_5Me_5)_4Ru_2S_2$ since it could be trapped chemically.[10]

In the preceding examples one can see that the organic coligands control the condensation pathway for desulfurization reactions. A pair of cyclopentadienyl ligands leads to cyclic oligomers while monocyclopentadienyl compounds give clusters. It is interesting to consider the desulfurization of polysulfido complexes *unconstrained* by spectator ligands. This approach could define novel routes to inorganic materials via molecular precursors. The resulting inorganic solids would in their simplest form have the formulae MS_x ($x \geq 1$) although ternary and higher order phases are possible. Such species could find application in catalysis, microelectronics, and as battery cathodes.

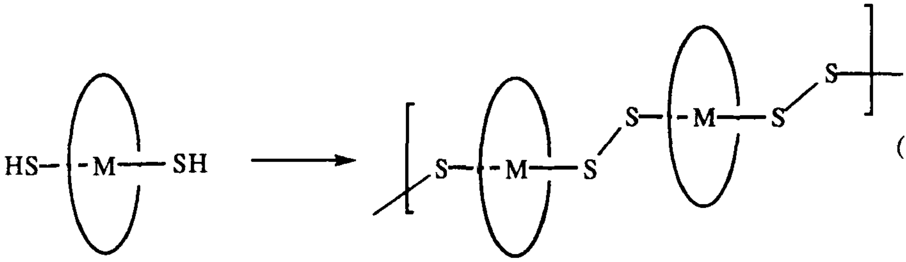
The desulfurization induced route to metal sulfides from polysulfido precursors exploits the *enhanced abilities of* S^{2-} *and* S_2^{2-} *to bridge several metals.* Sulfides and persulfides are well known for their ability to bridge many metals, examples being common in the area of mineralogy, e.g. pyrite (FeS_2) where the S_2 is bound to six iron atoms, troilite (FeS) where S is bound to six iron atoms, and wurtzite where S is bound to four zinc atoms. This analysis suggests that desulfurization induced oligomerization is driven not only by relief of ring strain (the case of $(RC_5H_4)_2TiS_2$) but also by the enhanced ligating power associated with S_x^{2-} where x is small.

In evaluating this problem, we have considered both transition metal and main group derivatives. A large number of potential precursors of the formula $ML_xS_y^z$ are known. Ideally coligands in such compounds confer solubility and stabilize the complex, but the same coligands must be readily eliminated upon polymerization. It is in this last requirement that cyclopentadienyl ligands fail. An obvious and attractive class of stabilizing spectator ligands are neutral amine bases, such as pyridine (py) and n-methylimidazole (MeIm). Examples of charge-neutral metal complexes of this type of complex are not common but they include $Cu_4(S_5)_2(MeIm)_4$ and $ZnS_6(py)_2$.[11] Our studies show that such complexes deposit binary metal sulfides when treated with sulfur abstracting agents.[12] Anionic metal polychalcogen compounds are particularly numerous and they represent viable precursors to inorganic polymers. This approach is illustrated by Kanatzidis' finding that the deselenization of $Cd(Se_4)_2^{2-}$ leads to deposition of CdSe.[13]

Main group polychalcogen compounds are dominated by anionic species, e.g. $Sb_2S_{14}^{2-}$.[14] This trend may reflect the relatively higher electronegativities associated with the main group elements. Desulfurization of the binary carbon sulfides such as C_3S_8 and C_6S_9 appears also to lead the formation of polymers.[15]

PART II. FERROCENEPOLYSULFIDES DERIVED FROM FERROCENE TRISULFIDES

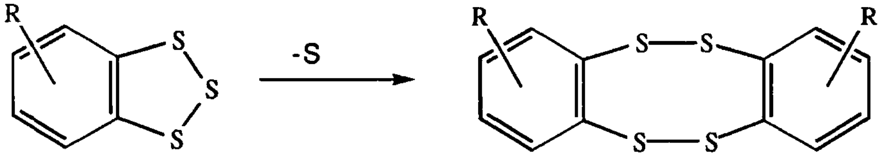
One way to generate metal polysulfido polymers would be to fix oligosulfur ligands trans on a metal center. For example, it is likely that polymers could be prepared by oxidative dehydrogenation of *trans*-$ML_2(SH)_2$ or better, from related hexacoordinated complexes such as $M(mac)(SH)_2$ (mac = porphyrin, etc), eq. 3.



(3)

This remains an interesting goal, the demanding aspect being the preparation of trans dithiols whose M-S bonds could survive the polymerization conditions. Additionally one must select metals that tend not to form M=S or M(η^2-S_2) species.

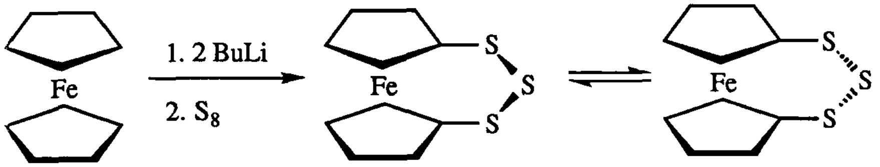
Alternatively, polymers could in principle be prepared via the desulfurization of *ligands* bearing (noncoordinated) polysulfide linkages. Many organic polysulfides are known and one can envision species which feature both a conventional donor site and a polysulfide. Complexation of the donor to the metal affords the monomer which upon desulfurization converts to an oligosulfide. The benzene nucleus provides an attractive scaffold for affixing both the polysulfide and the donor center. Unfortunately, desulfurization of benzopolysulfides seems to give mainly dimers.[16] The problem here is that like the titanocene case, the sulfur atoms are constrained to remain cis (eq. 4).



(4)

For these reasons we searched for sulfur-rich ligands that will tend to rotate upon cleavage of the S-S bonds. This requirement is met by the metallocenes where the cyclopentadienyl groups are known to rotate with very low barriers.

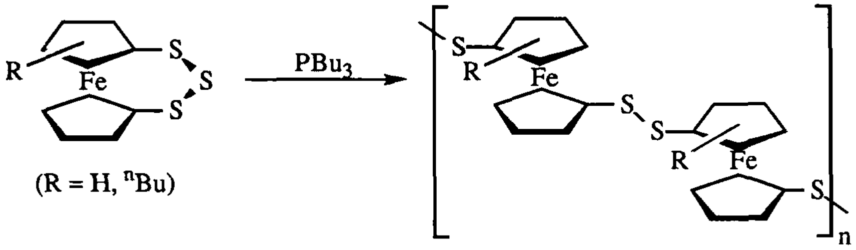
The ferrocene trisulfides were identified by us as potential precursors to polymers. These species can be efficiently prepared by direct lithiation of the metallocene followed by treatment with the elemental chalcogen. In addition to the trisulfides, compounds with Se_3, Te_3, and mixed chalcogen bridges are known, not to mention Ru and Os analogs. Such compounds have been heavily studied, primarily to elucidate the factors controlling conformation of the trichalcogen strap (eq. 5).[17]



(5)

We envisioned that removal of the central sulfur atom of the ferrocene trisulfides might lead to strained persulfide. If this strained molecule underwent S-S bond scission, this would allow rotation of the cyclopentadienyl rings and polymerization via reformation of strain free S-S bonds.

In 1992 we reported that PBu_3 reacts with a solution of $Fe(C_5H_4)_2S_3$ to deposit an orange solid with the composition $Fe(C_5H_4)_2S_2$. Because of its low solubility, the molecularity of this species could not be determined, although it seems unlikely to be monomeric. This point was verified by studies on Fe(*n*-BuC_5H_3)(C_5H_4)S_3, the first example of a substituted metallocene trisulfide. Desulfurization of this *n*-butyl compound afforded soluble persulfido linked polymers whose high molecular weights were confirmed by size exclusion chromatography (SEC) (eq. 6)[18]



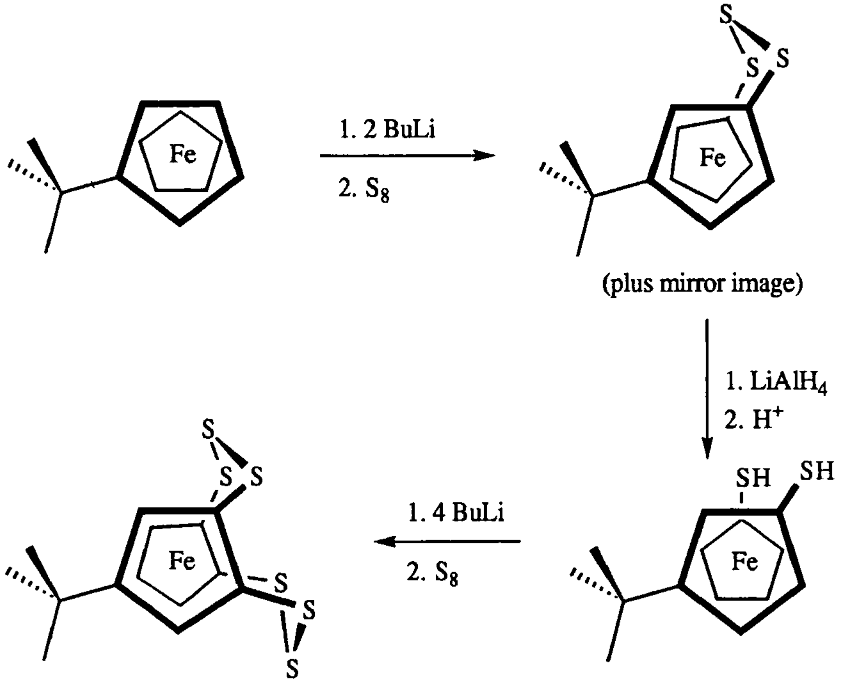
(6)

These initial studies were followed by a detailed report on the *t*-butyl-substituted polymers [Fe(*t*-$BuC_5H_3)_2S_2]_n$ and [Fe(C_5H_4)(*t*-BuC_5H_3)$S_2]_n$.[19] As originally envisioned this polymerization reaction appears to proceed via an initial desulfurization followed by interconnection of the metallocenes via persulfide linkages.

We should mention that the area of ferrocene-based polymers has been the subject of insightful studies by other groups. Noteworthy is the work of Herberhold, Nuyken, and their coworkers who prepared oligomeric ferrocenes via the radical initiated reaction of 1,1'-ferrocenedithiol with norbornadiene.[20] An extensive series of publications have described other main group bridged metallocene polymers formed via the thermal ring opening of strained ferrocenes such as $Fe(C_5H_4)_2E$, where E = SiR_2, GeR_2, and C_2H_4. The studies of Manners' and Pannell's groups are relevant to ours, the major difference is that they isolate the strained polymerizable precursor whereas we generate ours in situ.[21]

PART III. BIS(TRISULFIDO)-FERROCENES AND THEIR POLYMERIC DERIVATIVES

One approach to high molecular weight polymers involves the use of multiple polymerizable functional groups. Crosslinking groups for persulfido polymers could in principle be prepared from the higher order ($x > 1$) members of the ferrocene-polysulfides $Fe(C_5H_{5-x})_2(S_3)_x$. For this reason we have examined the bis(trisulfide) $Fe(C_5H_3)_2(S_3)_2$.[22] This species can be prepared by tetralithiation of 1,1'-ferrocenedithiol followed by sulfurization with S_8. This transformation involves deprotonation of the thiol groups followed by metalation adjacent to the thiolates on each of the rings. The same overall procedure was conducted starting with *t*-butylferrocene (Scheme 2).



SCHEME 2

These syntheses hinge on the ring metalation of the ferrocenedithiolate, which is based on the finding of Figuly and Martin that thiophenols undergo ortho-metalation with BuLi.[23] The tetralithiated intermediate was not isolated but is directly oxidized with sulfur. An extractive work up gives 1,1',2,2'-$Fe(C_5H_3)_2(S_3)_2$ in ca. 20% yield. The structure of this compound has been established by single crystal X-ray diffraction.[24] The regiochemistry observed for the metalation of the *t*-Bu substituted ferrocene has been observed previously.[25]

^{1}H NMR measurements of freshly prepared solutions of $Fe(C_5H_3)_2(S_3)_2$ exhibit an A_2B spin system consistent with a structure having C_{2v} symmetry with eclipsed cyclopentadienyl rings. Signals assigned to this species diminish over several minutes with concurrent growth of three new signals. These new signals are assigned to a conformer of C_s symmetry, giving an ABC coupling pattern. The isomerization conforms to a mechanism in which the central sulfur of one tri-sulfide bridge flips to the opposing side resulting in "bridge reversal". The A_2B and ABC spin systems for the two isomers were verified by ^{1}H-^{1}H correlation NMR measurements. ^{1}H NMR measurements show that the same equilibrium applies to $Fe(t\text{-}BuC_5H_2)(C_5H_3)(S_3)_2$: fresh solutions feature a single CH_3 resonance as well as a singlet and an A_2B pattern for the other protons. Upon standing, new signals appear that can be assigned to the C_1 conformer, which is chiral.

Recrystallization of equilibrated samples of the bis(trisulfides) gives only the symmetric conformers. A typical recrystallization is done over several hours by cooling a saturated THF solution. The $t_{1/2}$ for isomerization based on the k_{-1} values (see below) are ~ 20 min. at room temperature. As expected, flash evaporation of an equilibrated THF solution gives a mixture of the conformers, the rate of solvent removal in this case being faster than the rate of isomerization.

Rates of isomerization for the bis(trisulfides) were determined from ^{1}H NMR measurements. The isomerization was found to follow reversible first order process, described by the following rate equation:

$$\ln\left[\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}}\right] = -(k_1 + k_{-1})t$$

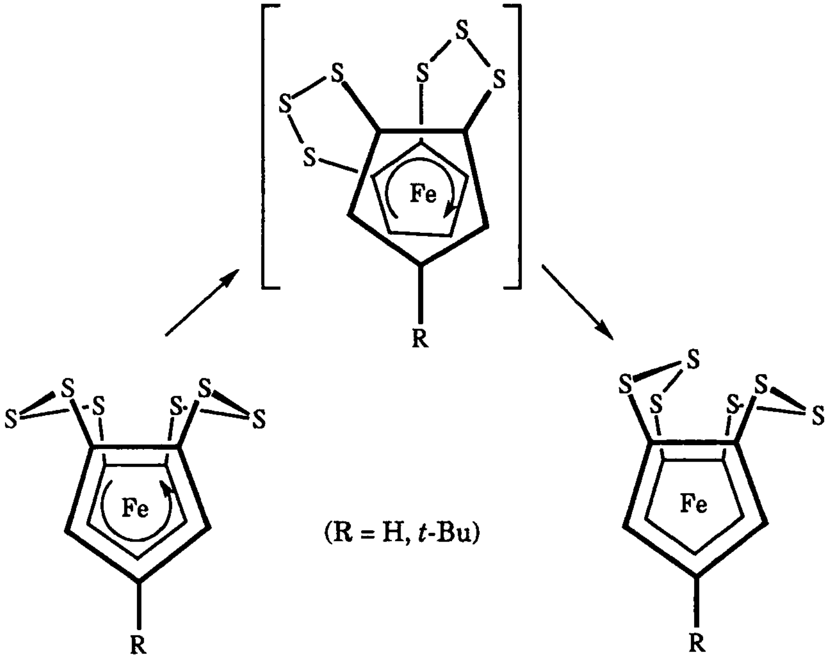
Plots of ln $([A] - [A]_{eq})/([A]_o - [A]_{eq})$ vs. time were linear with slope $(k_1 + k_{-1})$. This value together with the equilibrium constant allowed us to calculate both k_1 and k_{-1} (Table I). The rate constants for the inversion of individual S_3 bridges in the C_{2v} conformers are not identical to k_1 since the two trisulfide bridges are equivalent, and the inversion rate per trisulfide is half of the observed k_1.[26]

Abel et al have proposed that bridge reversal for the metallocene trichalcogenides occurs via the rotation about the C_5R_5 to Fe bond as well as flexing of the C-S-S and S-S-S angles to give a conformation in which the cyclopentadienyl rings are staggered (Scheme 3). The intermediate structure resembles the half-chair conformation of cyclohexane.

TABLE I. Kinetic and thermodynamic data for the hexasulfides and related trisulfides

	k_1 (s^{-1})	k_{-1} (s^{-1})	K_{eq}	0.5k_1 (s^{-1})	$\Delta G^{\ddagger a}$
$Fe(C_5H_3)_2(S_3)_2$	6.5×10^{-4}	7.0×10^{-4}	0.93	3.25×10^{-4}	91^b
$Fe(C_5H_3)(t\text{-}BuC_5H_2)(S_3)_2$	4.5×10^{-4}	4.9×10^{-4}	0.92	2.25×10^{-4}	92^c
$Fe(C_5H_4)_2S_3$	5.0×10^{-2}				80.4^d
$(CH_2)_3S_3$	6.6×10^1				55.4^e

[a] kJ/mol; [b] T = 18.9 °C; [c] T = 18.7 °C, ;[d] T = 25 °C [26d]; [e] T = -8 °C [27]



SCHEME 3

The bridge reversal barriers for the bis(trisulfides) are higher than that reported for monotrisulfides (Table I). These higher values likely result from the greater torsional strain placed on the molecule by the requirement that bonds in both trisulfide groups must distort during isomerization. The ^1H NMR signals for $Fe(C_5H_3)_2(S_3)_2$ (d_5-nitrobenzene, 200 MHz) coalesce into two broad bands at 150 °C, further demonstrating the conformational isomerism of this molecule. Presumably at somewhat higher temperatures, not attainable by our instrument, the spectrum would consist of a doublet and a triplet.

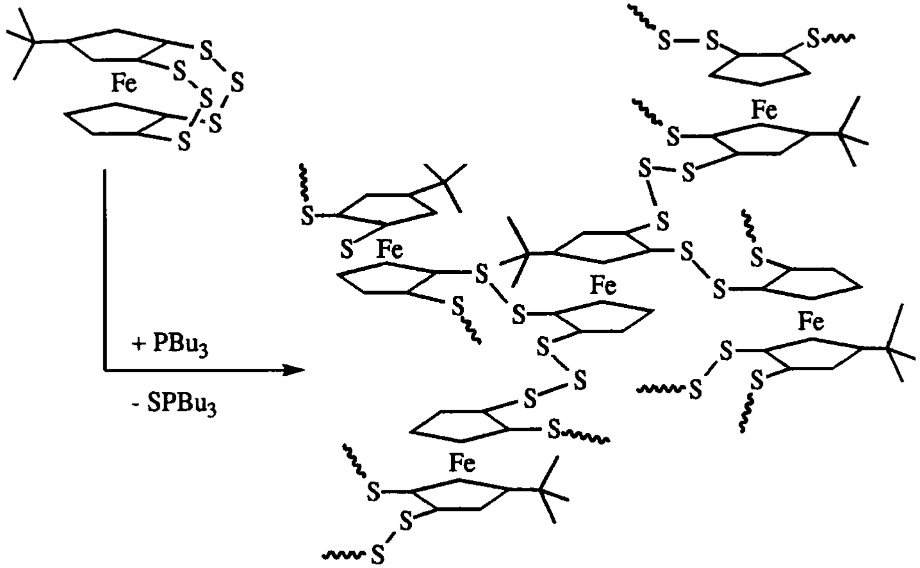
The addition of a trisulfide bridge to ferrocene is known to shift the redox couple to higher oxidation potentials.[28] As expected, the addition of a second trisulfide bridge also has a profound effect. Cyclic voltammetric measurements show that the $E_{1/2}$ values for the bis(trisulfides) are approximately 500 mV more positive than for the parent ferrocene (Table II). While the presence of one trisulfide bridge increases the $E_{1/2}$ by over 300 mV, a second trisulfide bridge shifts the potential to a lesser degree (~ 170 mV).

TABLE II. Redox Potentials of Selected Ferrocenes (vs. Ag/AgCl).

Substituted Ferrocene	$E_{1/2}$ (mV)
$Fe(C_5H_5)_2$	542
$Fe(C_5H_4)_2S_3$	857
$Fe(C_5H_3)_2(S_3)_2$	1025
$Fe(t\text{-}BuC_5H_4)(C_5H_5)$	481
$Fe(t\text{-}BuC_5H_3)(C_5H_4)S_3$	806
$Fe(t\text{-}BuC_5H_2)(C_5H_3)(S_3)_2$	975

Finally we turn to the polymerization of the ferrocene bis(trisulfides). The reaction of 2 equivs of PBu_3 and $Fe(C_5H_3)_2(S_3)_2$ produces a bright orange solid with an Fe:S ratio of ~1:4. This material could not be obtained in analytical purity, perhaps due to some entrapment of PBu_3 or $SPBu_3$ in the polymeric network. Evaluation of the molecular weight distribution of this material was precluded by its complete insolubility in organic solvents.

Treatment of the $Fe(t\text{-}BuC_5H_2)(C_5H_3)(S_3)_2$ with PBu_3 gives orange *solutions* of polymeric species whose molecular weight distributions proved very sensitive to the reaction conditions. With 1.5 equiv PBu_3, we observed the clean conversion of the phosphine to $SPBu_3$ (^{31}P NMR spectroscopy). As indicated by SEC analysis , the initial molecular weights distribution ranges from ~8,000 to > 5 x 10^6 daltons. Over a period of several minutes, very large molecular weight species appear in the SEC traces. Based on peak intensities, the high molecular weight fractions account for approximately 50% of the monomer units. Because the polymer cannot be redissolved once the solvent is removed, the reaction solutions containing $[Fe(t\text{-}BuC_5H_2)(C_5H_3)(S_{3-x})_2]_n$ (x = 0, 1) were purified by preparative-scale SEC; this allowed the easy removal of the low molecular weight fractions including $SPBu_3$. A recent reanalysis of the SEC data indicates that the purified polymer, which is highly polydisperse, has an $M_n \approx 7.4 \times 10^4$ and $M_w \approx 2.1 \times 10^6$. The very large molecular weights are extremely unusual for organotransition metal network polymers and are attributed to the crosslinking capability of the polyfunctional monomer. The structure proposed for this network is shown in Scheme 3.



SCHEME 3

ACKNOWLEDGEMENTS

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