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Articles

Ferrocenyl Derivatives with One, Two, or Three Sulfur-Containing Arms for Self-Assembled Monolayer Formation

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Self-assembled monolayers of electroactive molecules can form on gold electrodes if the molecules include a sulfur-containing group to coordinate with the gold surface. We have prepared a molecule with a tripod of sulfur groups that has the potential of fixing the geometry of the molecule relative to the gold surface. The target (**3**) contained the good one-electron donor ferrocene connected through a benzene spacer to an isobutane tripod, with each arm of the tripod ending in a methylthio group. Analogous compounds with one (**1**) and two (**2**) coordinating arms were also prepared.

Introduction

Molecules that include a sulfur-containing group, such as thiols (R−S−H), disulfides (R−S−S−R), or sulfides (R−S−R), can spontaneously form self-assembled monolayers (SAMs) on a gold surface when the sulfur coordinates with the gold.[1] Long alkyl chains tend to promote stability in SAMs, by increasing interchain van der Waals forces.[2] These chains can also serve as tethers for electroactive end groups, such as ferrocene, which can be detected electrochemically by using the gold surface as an electrode.[3] Ferrocene is an excellent one-electron donor which exhibits a reversible cyclic voltammogram.[4]

We have been interested in preparing SAMs of electroactive donor−σ−acceptor systems. One question that arises is the orientation of the electroactive group with respect to the surface. Measurements indicate that simple alkanethiols form closely packed monolayers at a 30° angle to the gold surface.[5] But molecules of nonuniform shape may form less-ordered SAMs. The electroactive end groups may be able to approach closer to the electrode, as has been suggested for silane-tethered groups,[6] perhaps at tilt domain boundaries.[7] Such excursions could influence the observed electrochemistry.

We sought to prepare a molecule with a tripod of anchoring sulfur groups. By using a rigid isobutane tripod, the electroactive group would be fixed in distance and in geometry, with its molecular axis perpendicular to the electrode surface. Three-point anchoring, rather than van der Waals interactions, would then control the geometry of the SAM. For comparison, we also sought analogues with two coordinating anchors,[8] whose movement would be constrained to swinging back and forth in one dimension, and analogues with one anchor, which would enjoy the capability of complete two-dimensional movement. Variations in electrochemical properties could be sought with such compounds.

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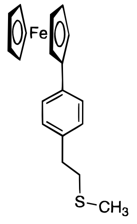
We report here the preparation of a ferrocene anchored by three methyl sulfide groups (**3**), along with the analogous two- and one-arm anchored sulfides (**2** and **1**, respectively). Thiols would be preferable coordinating groups, as they form SAMs much more robustly than sulfides;[9−12] however, they can be difficult to work with due to their tendency to oxidize or act as nucleophiles. This turned out to be the case here: although we were able to prepare the corresponding one-armed thiol **4**, we have so far been unable to isolate the two-armed thiol **5** in pure form.



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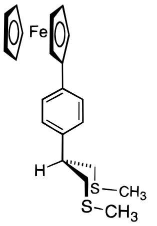

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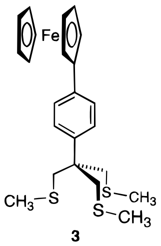

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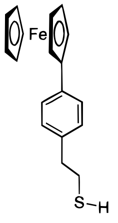

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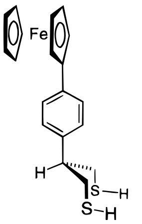

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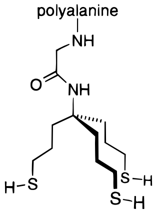

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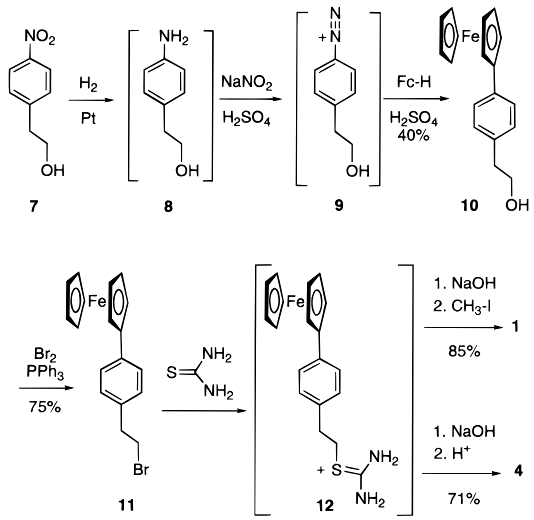
A three-armed thiol (**6**) based on a tripropyl methylamine tripod has been used to attach polyalanine to a gold surface.[13] Further, a derivative with three of these tripods attached to one polyalanine provided nine points of attachment. The extra methylenes in these compounds allow potential flexibility that is avoided in compound **3**.

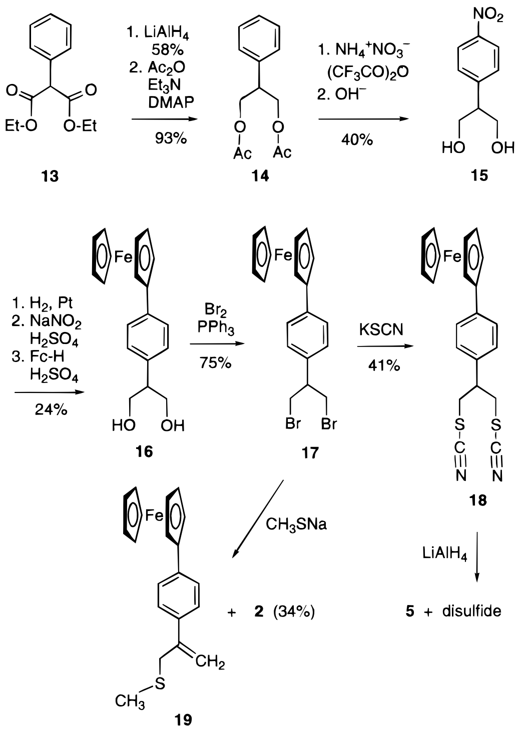
Results and Discussion

Initial attempts to connect ferrocene directly to an isobutane tripod failed and prompted us to include a benzene ring as a spacer. To attach the ferrocene donor to the phenyl spacer, we employed the diazonium coupling reaction of aryl diazonium salts to ferrocene/ferrocenium mixtures in sulfuric acid.[14] Thus, 2-(4-ferrocenylphenyl)ethanol (**10**) could be prepared from diazotized **8**, which was obtained by catalytic hydrogenation of **7** (Scheme 1). Alcohol **10** was converted to bromide **11** with bromine and triphenylphosphine,[15] and thence to the thiouronium salt **12**. Conversion of **12** to the one-armed analogues methyl sulfide **1** and thiol **4** proceeded in good yields as shown in Scheme 1.

Scheme 1



Scheme 2



Scheme 2 shows the route to two-armed analogues. Literature procedures were followed to obtain **14**: reduction[16a,b] of phenylmalonate (**13)** gave 2-phenyl-1,3-propanediol, which was protected[18] as the diacetate **14**. Following nitration, the acetate groups were removed to improve solubility for the aqueous ferrocene coupling reaction, giving diol **15**. Catalytic hydrogenation of the nitro group, diazotization, and ferrocene coupling gave **16**. Conversion of hydroxyls to bromides proceeded as before to give **17**, but the direct displacement of bromide with thiomethoxide was much preferable in this case to the thiourea method in producing the two-armed bissulfide ferrocene **2**. An apparent side reaction in this last step was elimination of HBr, leading to the formation of

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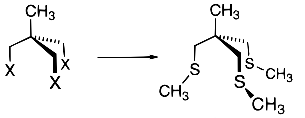
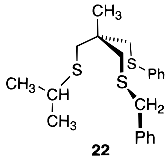
alkene **19**, which was removed chromatographically. At high reaction temperatures, **19** became the major product.

Treatment of the dibromide **17** with thiocyanate produced the bisthiocyanate **18**, and reduction with $LiAlH_4$ gave a crude product whose spectra were consistent with the two-armed dithiol ferrocene **5**. However, chromatographic purification attempts appeared to cause polymerization and/or cyclization, and we were unable to isolate pure **5** for analysis.

Difficulty might be expected in using these straightforward synthetic approaches to incorporate the three required sulfur groups into a sterically congested target like **3**. S_N2 reactions capable of placing three sulfurs in the required neopentyl positions are known, however. For example, excess methanethiolate can convert **20** (X = Cl[19] or X = Br[20]) to **21**; ethanethiolate can also be used.[21] Thiocyanate can displace the tosylates of **23** to form **24**.[22] Similarly, the hexasulfide **25** has been prepared from **23** for use as a hexa-coordinating "supertripodal" ligand.[23,24] Even the congested, chiral tris-sulfide **22** can be prepared by sequential displacement steps on a suitable precursor.[25] These successes suggested that a route to **3** through the key tribromo intermediate **30** might be feasible.



20 **21**



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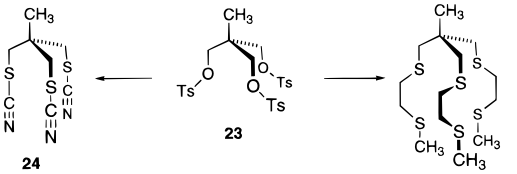
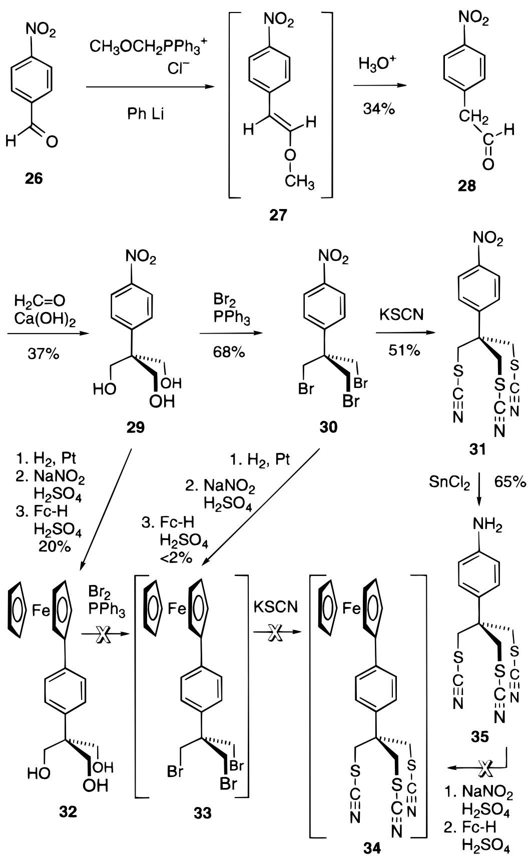


24 **23** **25**

The Wittig reaction[26] of 4-nitrobenzaldehyde with (methoxymethyl)triphenylphosphonium chloride gave nitrophenylacetaldehyde **28**, which was subjected to a Tollens condensation[27−29] (a double aldol addition of formaldehyde followed by a Cannizzaro reduction with formaldehyde as the hydride donor) to give the triol **29**,[30] as shown in Scheme 3. Bromination proceeded as before to give the tribromide **30**.

Displacement of the three bromines with thiocyanate was successful, giving **31**, and reduction to the aniline **35** was accomplished with $SnCl_2$. However, the ferrocene coupling reaction of the corresponding diazonium salt did not result in significant amounts of product **34**. A likely cause of the difficulty was the low solubility of **35** in the aqueous coupling medium.

Scheme 3



We then attempted to perform the coupling before the thiocyanations. Hydrogenation of **30**, followed by diazotization and ferrocene coupling, resulted in a <2% yield of **33**, again probably due to solubility problems, and analysis of the product mixture following treatment of **33** with thiocyanate indicated cleavage of the ferrocene from the benzene spacer group rather than formation of **34**.

We next attempted to perform the ferrocene coupling on the aniline derived from triol **29**; its improved water solubility allowed isolation of the coupled product **32** in 20% yield. However, attempted bromination of **32** resulted in decomposition of the ferrocene, as indicated by loss of ferrocene signals in the NMR spectrum of crude material.

Thiomethoxide was capable of adding three methylthio groups to **30** (Scheme 4). (A side reaction appeared to be denitration, judging from the shielded aromatic NMR signals of a byproduct chromatography fraction; nitro groups are known to be potential leaving groups in nucleophilic aromatic substitutions.[31]) Reduction with $SnCl_2$,[32] diazotization, and ferrocene coupling provided the target three-armed ferrocene **3**, albeit in low yield.

Analysis of self-assembled monolayers of **1**−**3** will be reported elsewhere.

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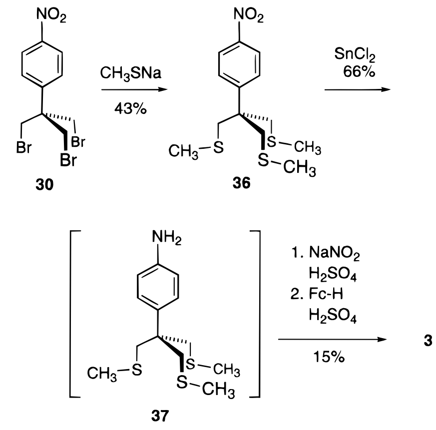
Scheme 4



Experimental Section

General Methods. Starting materials and reagents were purchased from Aldrich unless otherwise noted. Column chromatography was performed using E. Merck silica gel, 230–400 mesh. Melting points are not corrected. Elemental analyses were carried out by Desert Analytics, Tucson, AZ.

2-(4-Ferrocenylphenyl)-1-ethanol (10). 2-(4-Nitrophenyl)-1-ethanol (**7**, 16.7 g, 100 mmol) was dissolved in 150 mL of EtOH. Pt/C (100 mg) was added, and the mixture was shaken under 40–60 psi of H_2 for 2 h. The catalyst was removed by filtration, and the solvent was removed by rotary evaporation, giving a quantitative crude yield of 2-(4-aminophenyl)-1-ethanol (**8**). This material was dissolved in 30% H_2SO_4, and sodium nitrite (8.3 g, 0.12 mol) in water was added dropwise at 0 °C. After 15 min of stirring, the resulting diazonium salt (**9**) was used as follows.

A mixture of 37.2 g (200 mmol) of ferrocene in 50 mL of concd H_2SO_4 was left standing overnight and then was poured into sufficient ice water to make the H_2SO_4 concentration 30%. The diazonium salt solution was added to the resulting blue ferrocenium solution. The solution was kept at 0 °C for 15 h and then was neutralized with 20% sodium hydroxide and extracted with EtOAc. The organic layer was dried with $MgSO_4$ and concentrated by rotary evaporation. Column chromatography (1:3 EtOAc:hexanes) gave a 40% yield of **10** as a dark red powder, mp 93–94 °C. ^1H NMR ($CDCl_3$): δ 7.43 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 8.2$ Hz, 2H), 4.61 (t, $J = 1.8$ Hz, 2H), 4.30 (t, $J = 1.8$ Hz, 2H), 4.15 (s, 1H), 4.04 (s, 5H), 3.87 (t, $J = 6.4$ Hz, 2H), 2.85 (t, $J = 6.4$ Hz, 2H). IR: 3252 cm^{-1}. The analytical sample was crystallized from hexanes. Anal. Calcd for $C_{18}H_{18}FeO$: C, 70.61; H, 5.93. Found: C, 70.88; H, 5.83.

2-(4-Ferrocenylphenyl)-1-bromoethane (11). To a suspension of 3.94 g (15.0 mmol) of triphenylphosphine in 30 mL of dry acetonitrile was added bromine (2.40 g, 15.0 mmol) dropwise at 0 °C under nitrogen. After 10 min, 3.06 g (10.0 mmol) of **10** in 10 mL of acetonitrile was added dropwise. The resulted solution was refluxed for 4 h, and then extracted with hexanes. Column chromatography (1:20 EtOAc:hexanes) gave a 90% yield of **11** as a dark red solid, mp 76–77 °C. ^1H NMR ($CDCl_3$): δ 7.42 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 8.2$ Hz, 2H), 4.62 (t, $J = 1.6$ Hz, 2H), 4.31 (t, $J = 1.6$ Hz, 2H), 4.04 (s, 5H), 3.58 (t, $J = 7.7$ Hz, 2H), 3.14 (t, $J = 7.7$ Hz, 2H). The analytical sample was crystallized from hexanes at −78 °C. Anal. Calcd for $C_{18}H_{17}BrFe$: C, 58.58; H, 4.64; Br, 21.65. Found: C, 58.80; H, 4.65; Br, 21.30.

2-(4-Ferrocenylphenyl)-1-(methylthio)ethane (1). Bromide **11** (369 mg, 1.00 mmol) and thiourea (761 mg, 10.0 mmol) were dissolved in 5 mL of DMSO. After 15 h, the mixture was cooled on an ice bath and basified to pH 11–12 with 10% NaOH. After 15 min at room temperature, the flask was returned to the ice bath, and 1.0 mL (16 mmol) of CH_3I was added dropwise. After 2 h at room temperature, the mixture was extracted with Et_2O; rotary evaporation of the solvent gave an 85% yield of **1** as a dark red powder, mp 79–80 °C. ^1H NMR ($CDCl_3$): δ 7.29 (d, $J = 8.2$ Hz, 2H), 7.11 (d, $J = 8.2$ Hz, 2H), 4.60 (t, $J = 1.9$ Hz, 2H), 4.27 (t, $J = 1.9$ Hz, 2H). 4.02 (s, 5H), 2.85 (m, 2H), 2.75 (m, 2H), 2.12 (s, 3H). Anal. Calcd for $C_{19}H_{20}FeS$: C, 67.86; H, 5.99; S, 9.53. Found: C, 67.80; H, 6.03; S, 9.38.

2-(4-Ferrocenylphenyl)-1-ethanethiol (4). Compound **11** (1.85 g, 5.01 mmol) and thiourea (761 mg, 10.0 mmol) were dissolved in 20 mL of DMSO. The solution was stirred for 1 day at room temperature. NaOH (20%) was added dropwise until the pH was 11–12. The solution was then acidified with hydrochloric acid and extracted with Et_2O. After rotary evaporation of the solvent, **4** was recrystallized from hexanes at −78 °C to give a 71% yield of a dark red solid, mp 59–60 °C. ^1H NMR ($CDCl_3$): δ 7.42 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 4.61 (t, $J = 1.7$ Hz, 2H), 4.30 (t, $J = 1.7$ Hz, 2H), 4.04 (s, 5H), 2.97–2.79 (m, 4H), 1.41 (t, 1H). IR (KBr): 2562 cm^{-1}. Anal. Calcd for $C_{19}H_{18}FeS$: C, 67.09; H, 5.63; S, 9.95. Found: C, 67.36; H, 5.37; S, 9.94.

2-(4-Nitrophenyl)propane-1,3-diol (15). 1,3-Diacetoxy-2-phenylpropane[18] (**14**, 1.18 g, 5.00 mmol), trifluoroacetic anhydride (4.20 g, 20.0 mmol), and ammonium nitrate (405 mg, 5.06 mmol) were put in 10 mL of dry $CHCl_3$ and reacted at 0 °C for 2 h and then at room temperature for 10 h. The mixture was poured into ice–water and extracted with $CHCl_3$. The organic layer was dried with $MgSO_4$ and concentrated by rotary evaporation, giving a 96% crude yield of 1,3-diacetoxy-2-(4-nitrophenyl)propane.

The crude nitroarene was dissolved in 20 mL of 5% NaOH in 50% aqueous ethanol, refluxed for 1 day, and extracted with EtOAc. The organic layer was dried with $MgSO_4$, concentrated by rotary evaporation, and purified by column chromatography (1:3 EtOAc:hexanes) to give a 40% yield of **15** (based on compound **14**) as a white solid, mp 98–99 °C. ^1H NMR (DMSO-d_6): δ 8.15 (d, $J = 8.6$ Hz, 2H), 7.53 (d, $J = 8.6$ Hz, 2H), 4.70 (t, $J = 5.2$ Hz, 2H), 3.74–3.61 (m, 4H), 2.98 (m, 1H). IR: 3538, 3254 cm^{-1}. Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 55.12; H, 5.50; N, 7.12.

2-(4-Ferrocenylphenyl)propane-1,3-diol (16). Treatment of 3.55 g (18.0 mmol) of nitroarene **15** with the procedure used to prepare **10** gave a 24% yield of dark red **16**, mp 135–136 °C. ^1H NMR ($CDCl_3$): δ 7.43 (d, $J = 8.1$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 4.62 (t, $J = 1.8$ Hz, 2H), 4.32 (t, $J = 1.8$ Hz, 2H), 4.05 (s, 5H), 3.98 (m, 4H), 3.10 (m, 1H), 1.99 (t, $J = 5.6$ Hz, 2H). IR: 3265 cm^{-1}. Anal. Calcd for $C_{19}H_{20}FeO_2$: C, 67.88; H, 6.00. Found: C, 68.18; H, 6.00.

2-(4-Ferrocenylphenyl)-1,3-dibromopropane (17). To a suspension of triphenylphosphine (1.44 g, 5.49 mmol) in 10 mL of dry acetonitrile was added bromine (0.88 g, 5.5 mmol) in 5 mL of acetonitrile dropwise under nitrogen at 0 °C. After 10 min, the diol **16** (603 mg, 1.79 mmol) in 5 mL of acetonitrile was added dropwise. The resulting solution was refluxed for 1.5 h and then extracted with hexanes. The organic layer was concentrated by rotary evaporation and purified by column chromatography (1:20 EtOAc:hexanes) to give a 90% yield of **17** as a dark red solid, mp 145–146 °C. ^1H NMR ($CDCl_3$): δ 7.45 (d, $J = 8.3$ Hz, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 4.62 (t, $J = 1.8$ Hz, 2H), 4.31 (t, $J = 1.8$ Hz, 2H), 4.04 (s, 5H), 3.77 (m, 4H), 3.36 (m, 1H). Anal. Calcd for $C_{19}H_{18}Br_2Fe$: C, 49.40; H, 3.93; Br, 34.59. Found: C, 49.73; H, 3.83; Br, 34.44.

2-(4-Ferrocenylphenyl)-1,3-dithiocyanopropane (18). Compound **17** (500 mg, 1.08 mmol) and potassium thiocyanate (1.94 g, 20.0 mmol) were refluxed in 20 mL of ethylene glycol dimethyl ether for 4 h. Water (100 mL) was added, and the mixture was extracted with EtOAc. Rotary evaporation of the $MgSO_4$-dried organic phase and purification by column chromatography (1:4 EtOAc:hexanes) afforded a 41% yield of **18**, mp 154–155 °C. ^1H NMR ($CDCl_3$): δ 7.45 (d, $J = 8.3$ Hz, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 4.62 (t, $J = 1.8$ Hz, 2H), 4.31 (t, $J = 1.8$ Hz, 2H), 4.04 (s, 5H), 3.83–3.71 (m, 4H), 3.40–3.31 (m, 1H). IR (KBr): 2148, 2072. Anal. Calcd for $C_{21}H_{18}FeN_2S_2$: C, 60.29; H, 4.34; N, 6.60; S, 15.33. Found: C, 60.17; H, 4.27; N, 6.54; S, 15.32.

2-(4-Ferrocenylphenyl)-1,3-bis(methylthio)propane (2). Sodium thiomethoxide (350 mg, 5.00 mmol) was added to a solution of dibromide **17** (924 mg, 2.00 mmol) in 10 mL of DMF.

After standing at room temperature overnight, the solution was poured into 100 g of ice and 100 mL of 10% HCl. The mixture was extracted with Et_2O, and the organic layer was dried with $MgSO_4$, concentrated by rotary evaporation, and purified by column chromatography (1:100 EtOAc:hexanes) to give a 34% yield of **2** as a dark red solid, mp 85−86 °C. ^1H NMR ($CDCl_3$): δ 7.43 (d, $J = 8.2$ Hz, 2H), 7.15 (d, $J = 8.2$ Hz, 2H), 4.62 (t, $J = 1.9$ Hz, 2H), 4.29 (t, $J = 1.9$ Hz, 2H), 4.03 (s, 5H), 3.00−2.83 (m, 5H), 2.03 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 140.3, 137.9, 127.6, 126.2, 85.2, 69.6, 68.8, 66.4, 45.2, 39.9 (CH_2), 16.3. Anal. Calcd for $C_{21}H_{24}FeS_2$: C, 63.63; H, 6.10; S, 16.18. Found: C, 63.73; H, 6.14; S, 16.20. Evidence for the formation of 2-(4-ferrocenylphenyl)-3-methylthio-1-propene (**19**) as a byproduct was afforded by ^1H NMR ($CDCl_3$) of a chromatography fraction: δ 7.43 (m, 4H), 5.50 (d, $J = 1.1$ Hz, 1H), 5.16 (d, $J = 1.1$ Hz, 1H), 4.63 (t, $J = 1.9$ Hz, 2H), 4.31 (t, $J = 1.8$ Hz, 2H), 4.05 (s, 5H), 3.58 (s, 2H), 2.06 (s, 3H).

4-Nitrophenylethanal (28). To a suspension of (methoxymethyl)triphenylphosphonium chloride (6.51 g, 19.0 mmol) in 50 mL of dry Et_2O at 0 °C was added phenyllithium (10 mL, 18 mmol, 1.8 M in hexanes) dropwise. After standing at room temperature for 4 h, the mixture was cooled again to 0 °C and 4-nitrobenzaldehyde (**26**, 907 mg, 6.00 mmol) was added in 10 mL of dry THF. After standing for 12 h at room temperature, the mixture was filtered and the filtrate was concentrated by rotary evaporation. The enol ether residue (**27**) was dissolved in 20 mL of EtOH, and 5 mL of 10% HCl was added. This mixture was refluxed for 3 h and then was extracted with Et_2O. The organic layer was dried with $MgSO_4$, concentrated by rotary evaporation, and purified by column chromatography to give a 35% yield of **28** as a pale yellow solid, mp 84−85 °C (lit.[33] mp 85−86 °C). ^1H NMR ($CDCl_3$): δ 9.82 (t, $J = 1.6$ Hz, 1H), 8.25 (d, $J = 1.8$ Hz, 2H), 7.41 (d, $J = 1.8$ Hz, 2H), 3.88 (d, $J = 1.6$ Hz, 2H).

2-(4-Nitrophenyl)-2-(hydroxymethyl)propane-1,3-diol (29). (4-Nitrophenyl)ethanal (**28**, 519 mg, 3.14 mmol), calcium hydroxide (934 mg, 12.6 mmol), and paraformaldehyde (378 mg, 12.6 mmol) were refluxed in 30 mL of THF for 3 days. The mixture was filtered, and the filtrate was concentrated by rotary evaporation and purified by column chromatography (3:1 EtOAc:hexanes) to give a 37% yield of **29** as an orange powder, mp 115−118 °C. ^1H NMR (DMSO-d_6): δ 8.14 (d, $J = 9.0$ Hz, 2H), 7.71 (d, $J = 9.0$ Hz, 2H), 4.60 (t, $J = 5.1$ Hz, 3H), 3.73 (d, $J = 5.1$ Hz, 6H). IR: 3487, 3413, 3325 cm^{-1}. Anal. Calcd for $C_{10}H_{13}NO_5$: C, 52.86; H, 5.77; N, 6.16. Found: C, 52.37; H, 5.49; N, 6.00.

2-(4-Nitrophenyl)-1,3-dibromo-2-(bromomethyl)propane (30). The procedure used to prepare compound **17** converted 1.39 g (6.13 mmol) of **29** to **30** as a white powder in 68% yield, mp 124−125 °C. ^1H NMR ($CDCl_3$): δ 8.27 (d, $J = 8.9$ Hz, 2H), 7.50 (d, $J = 8.9$ Hz, 2H), 3.95 (s, 6H). Anal. Calcd for $C_{10}H_{10}Br_3NO_2$: C, 28.88; H, 2.42; Br, 57.64; N, 3.37. Found: C, 28.88; H, 2.23; Br, 57.96; N, 3.25.

2-(4-Nitrophenyl)-1,3-dithiocyano-2-(thiocyanomethyl)propane (31). Compound **30** (2.30 g, 5.53 mmol) and potassium thiocyanate (9.72 g, 100 mmol) were heated at 100 °C in DMF for 10 h. Water (100 mL) was added, and the mixture was extracted with EtOAc. The organic layer was dried with $MgSO_4$ and concentrated by rotary evaporation. The residue was crystallized from 1:1 EtOAc:hexanes to give **31** in 51% yield, mp 163−164 °C. ^1H NMR (DMSO-d_6): δ 8.78 (d, $J = 8.9$ Hz, 2H), 7.94 (d, $J = 8.9$ Hz, 2H), 3.96 (s, 6H). IR (KBr): 2151 cm^{-1}. Anal. Calcd for $C_{13}H_{10}N_4O_2S_3$: C, 44.56; H, 2.88; N, 15.99; S, 27.45. Found: C, 44.60; H, 2.71; N, 15.78; S, 27.68.

2-(4-Ferrocenylphenyl)-2-(hydroxymethyl)propane-1,3-diol (32). The procedure used to prepare compound **10** (varied as follows: the diazonium salt was prepared in 25% H_2SO_4, and the ferrocenium solution was diluted to make 20% H_2SO_4) converted 1.24 g (5.50 mmol) of **29** to **32** in 20% yield; mp 161−162 °C. ^1H NMR (DMSO-d_6): δ 7.42 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 4.70 (t, $J = 1.8$ Hz, 2H), 4.42 (t, $J = 5.2$ Hz, 3H), 4.30 (t, $J = 1.8$ Hz, 2H), 4.03 (s, 5H), 3.72 (d, $J = 5.2$ Hz, 6H). IR (KBr): 3344 cm^{-1}.

2-(4-Nitrophenyl)-1,3-bis(methylthio)-2-(methylthiomethyl)propane (36). The procedure that was used to prepare compound **2** was employed on 2.16 g (5.19 mmol) of tribromide **30**, except that the reaction conditions were 0 °C for 3 h. Pale yellow needles of **36** were obtained in 43% yield, mp 51−52 °C. ^1H NMR ($CDCl_3$): δ 8.22 (d, $J = 9.0$ Hz, 2H), 7.57 (d, $J = 9.0$ Hz, 2H), 3.17 (s, 6H), 2.02 (s, 9H). Anal. Calcd for $C_{13}H_{19}NO_2S_3$: C, 49.18; H, 6.03; S, 30.30. Found: C, 49.13; H, 6.01; S, 30.37.

2-(4-Ferrocenylphenyl)-1,3-bis(methylthio)-2-(methylthiomethyl)propane (3). Tin(II) chloride dihydrate (4.51 g, 20.0 mmol) was added to a solution of 635 mg of nitroarene **36** (2.00 mmol) in 20 mL of dry EtOH. After the solution was refluxed for 12 h, 100 mL of 5% EDTA (aq) was added and the mixture was extracted with EtOAc. The organic layer was dried with $MgSO_4$ and concentrated by rotary evaporation to give a 66% yield of crude aniline **37**.

The ferrocene coupling procedure used to prepare compound **10** converted **37** to **3** as a dark red gum in 15% yield based on **36**. ^1H NMR ($CDCl_3$): δ 7.45 (d, $J = 8.6$ Hz, 2H), 7.29 (d, $J = 8.6$ Hz, 2H), 4.64 (t, $J = 1.9$ Hz, 2H), 4.30 (t, $J = 1.9$ Hz, 2H), 4.00 (s, 5H), 3.16 (s, 6H), 1.98 (s, 9H). Anal. Calcd for $C_{23}H_{28}FeS_3$: C, 60.51; H, 6.18; S, 21.07. Found: C, 60.76; H, 6.33; S, 21.44.

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Supporting Information Available: Experimental details for the preparation of compound **14** from **13** and the attempted syntheses of compounds **5** and **34**; IR spectral data for all compounds prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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