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Synthesis, Characterization, and Metal Complexation of Unsymmetrical 1,1′-Bis(organylthiolato)ferrocenes

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A series of new unsymmetrical 1,1′-disubstituted ferrocenediyl ligands featuring thioether substituents (SR, SR′ where R ≠ R′: Me, Ph, ^{t}Bu) have been conveniently synthesized via cleavage of ferrocenylsulfanes. The ligands display a range of coordination chemisty, exemplified by reaction with Pt, Pd, and W metal centers, and structural characterization indicates the bidentate, chelating nature of the ligands. Electrochemical studies show that the diferrocenyldisulfanes exhibit two separated one-electron oxidations where the mixed-valent monocations belong to the partially delocalized Robin-Day Class II, while for the metallocenophanes, chemical reversibility is noted along with some decomposition over time.

Introduction

The formation of unsymmetrical, multidentate ligands, focusing on aspects of hemilability,[1] continues to be of great interest. In particular, ferrocenyl and ferrocenediyl ligands are sought after due to their extensive coordination chemistry and applications within catalysis.[2,3] Ferrocene species with donor heteroatoms (e.g. P, N, S, O) substituted onto the cyclopentadienyl rings are well-known, especially those featuring homo-substitution (i.e. the same donor atom along with the same alkyl or aryl substituents) but much less well-known are unsymmetrical 1,1′-disubstituted ferrocenes featuring hetero-combinations of N, P, or S atoms, or R groups.[4] 1-(PR$_2$),1′-(SR)-ferrocenediyl ligands (R = alkyl, aryl) have been formed[5] and most recently by us[6] but as far as we are aware 1-(SR),1′-(SR′)-ferrocenediyl ligands are unknown where R ≠ R′ (alkyl or aryl). Bis(1′-organylthiolatoferrocenyl)disulfanes (R = *n*-butyl, phenyl) were first reported by Herberhold in 1991[7] via cleavage of the trisulfur bridge in 1,2,3-trithia-[3]-ferrocenophanes by organolithium reagents, followed by air oxidation. No further studies were reported, but we recognized that cleavage of the S−S bond in these disulfanes could potentially form unsymmetrical monoferrocenediyl ligands.

We report herein the convenient syntheses of novel unsymmetrical thioether-substituted ferrocenediyl ligands (where R ≠ R′: Me, Ph, ^{t}Bu) via cleavage of the analogous ferrocenyldisulfane species. Various methods have been investigated and compared and found to be dependent upon the nature of the R/R′ groups. Also included are examples of the coordination chemistry of the new ferrocenediyl ligands via reaction with palladium,

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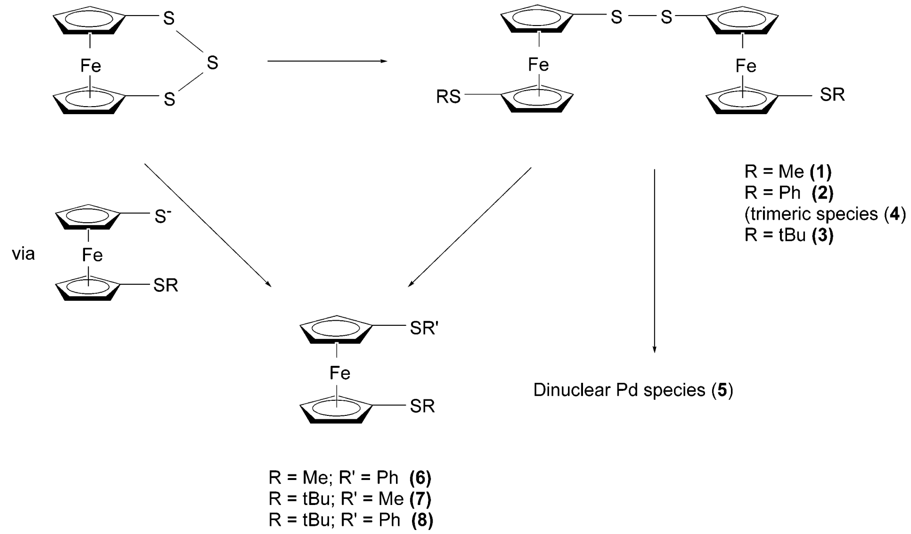
Scheme 1. Formation of Compounds 1−8



platinum, and tungsten metal centers, with full spectroscopic, electrochemical, and structural characterization.

Results and Discussion

I. Preparation of Bis(1′-organylthiolatoferrocenyl)disulfanes. The bis(1′-organylthiolatoferrocenyl)disulfanes, RS-Fc-SS-Fc-SR (where R = Me (**1**), Ph (**2**), and ^{t}Bu (**3**)) have all been prepared in a general, variable yielding synthesis (Scheme 1). A THF solution of 1,2,3-trithia-[3]-ferrocenophane was cooled to −78 °C, reacted with 2 equiv of the appropriate organolithium reagent, and stirred for 20 h. The reaction was exposed to the air, and water was added leading to a gradual lightening of the dark-red solution. The THF was removed under vacuum and the aqueous suspension extracted with dichloromethane. Column chromatography (neutral grade II alumina) gave a band due to unreacted 1,2,3-trithia-[3]-ferrocenophane followed by several other orange products, the first of which was the major product of the reaction, the desired bis(1′-organylthiolatoferrocenyl)disulfane. The methyl and phenyl derivatives (**1** and **2**) were isolated as deep orange oils, which solidified over time. The *tert*-butyl derivative was isolated as a flaky yellow/orange solid. All of the products are air stable and soluble in common organic solvents, but are only sparingly soluble in alcohols. The reaction with phenyllithium also gave isolable quantities of a yellow trimeric ferrocenediyl species containing two disulfide bridges (**4**) (Figure 1). Very small quantities of the analogous trimer were also found with the methyllithium and *tert*-butyllithium reactions but these were not isolated.

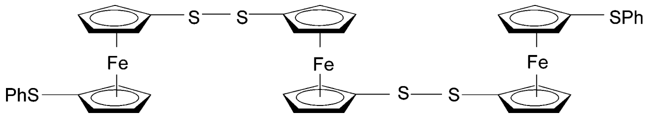


Figure 1. The trimeric species **4**.

The yields of the reactions to form **1**, **2**, and **3** were variable (the best being 40%, 25%, and 70% for R = Me, Ph, and ^{t}Bu, respectively) and seem to depend on the dilution and temperature of the reaction. Addition of water to the crude reaction mixture (to quench excess lithiating agents) before THF removal is crucial to obtain a pure product. Failure to do so results in a range of other monomeric and dimeric ferrocenediyl species, which are largely inseparable by column chromatography. For **1**−**3**, four pseudotriplets (an AA′BB′CC′DD′ splitting pattern) would be expected in the ^{1}H NMR spectra. However, as a result of closely overlapping signals, only the methyl derivative comes close to showing this pattern. The spectra show a highfield triplet and a downfield multiplet. For the *tert*-butyl derivative the multiplet is split into a triplet and a singlet.

Slow evaporation of a hexane solution of **1** gave yellow platy needles and the single-crystal X-ray analysis confirmed the structure and showed it to have a fairly extended geometry with approximate C_2 symmetry and a torsional twist of ca. 87° about the S−S linkage (Figure 2). The S(1)−S(2) bond length of 2.068(4) Å is typical of an S−S single bond. Both ferrocenediyl units have essentially eclipsed geometries with a stagger of the Cp rings of less than 3° for Fe(1) and ca. 5° for Fe(2), the C_5H_4 rings being inclined to each other by 3° in each case. The nonbonded S···S distances within each ferrocenediyl unit are both 3.56 Å. There are no intermolecular packing interactions of note.

II. Preliminary Studies of the Coordination Chemistry of Bis(1′-organylthiolatoferrocenyl)disulfanes. The bis(1′-organylthiolatoferrocenyl)disulfanes (**1**−**3**) synthesized have the potential to bind to metal centers in a variety of ways. The most likely donors are the thioether sulfur atoms. The size and flexibility of the ligands makes chelation of the two thioether substituents to one metal center unlikely and therefore oligomeric products may form. If chelates form then it will prove interesting to see the involvement (if

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5

	mol. A	mol. B		mol. A	mol. B
Pd−Cl	2.327(2)	2.326(2)	Pd−S(1)	2.3546(14)	2.3595(13)
Pd−S(2)	2.304(2)	2.306(2)	Pd−S(2A)	2.3025(12)	2.3106(12)
S(1)−C(1)	1.774(6)	1.752(5)	S(2)−C(6)	1.771(5)	1.781(5)
Cl−Pd−S(1)	102.25(6)	101.38(6)	Cl−Pd−S(2)	171.99(5)	172.90(6)
Cl−Pd−S(2A)	88.69(6)	89.52(6)	S(1)−Pd−S(2)	85.68(5)	85.48(6)
S(1)−Pd−S(2A)	168.96(7)	169.05(7)	S(2)−Pd−S(2A)	83.35(6)	83.66(6)
C(1)−S(1)−C(11)	104.8(3)	104.3(3)	C(1)−S(1)−Pd	105.1(2)	104.3(2)
C(11)−S(1)−Pd	120.2(3)	120.7(2)	C(6)−S(2)−PdA	102.7(2)	103.3(2)
C(6)−S(2)−Pd	104.7(2)	103.0(3)	PdA-S(2)−Pd	96.65(6)	96.34(6)

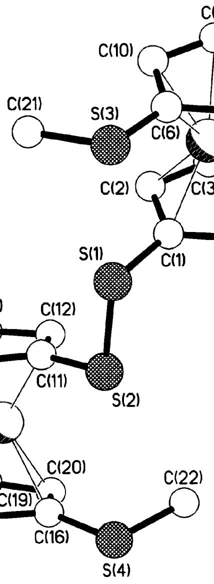

Figure 2. The molecular structure of **1**; the S(1)−S(2) bond length is 2.068(4) Å and the C(1)−S(1)−S(2) and S(1)−S(2)−C(11) angles are 103.6(4)° and 103.7(4)°, respectively.

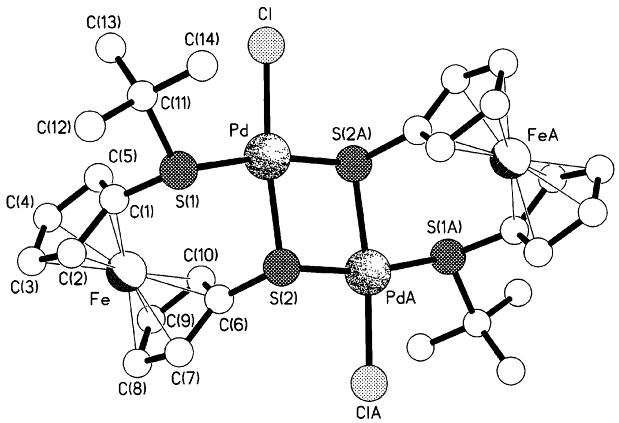

Figure 3. The molecular structure of one of the crystallographically independent centrosymmetric complexes in the crystals of **5**; the transannular Pd···Pd and S···S distances are 3.44 Å [3.44 Å] and 3.06 Å [3.08 Å], respectively, the values in square brackets relating to the second independent dimer.

any) of the disulfide bridge in the complex. The reaction of **3** with [Pd(PhCN)$_2$Cl$_2$] gave a small quantity of a dark-red precipitate (**5**), which was also soluble in polar solvents but insoluble in nonpolar solvents. Dark-brown needles suitable for X-ray diffraction were grown by slow evaporation of a chloroform solution and the X-ray analysis showed that the attempt to synthesize an extended *S*,*S*′ palladium chelate complex of **3** had proven unsuccessful. Instead an unusual insertion reaction into the S−S bond had occurred resulting in a structure reminiscent of that of a closely related mesityl-substituted analogue reported by us recently.[8] Crystals of **5** contain two crystallographically independent complexes, each with essentially identical geometries. The complex has crystallographic C_i symmetry and a planar central Pd_2S_2 ring (Figure 3), but with the chelating sulfur lone pairs on S(1) and S(2) both lying on the same side of the palladium coordination plane whereas in the related mesityl species the symmetry is C_2, the central Pd_2S_2 ring being folded with the chelating sulfur lone pairs lying on opposite sides.[8] The geometry at palladium is distorted square planar with cis angles in the range 83.35(6) to 102.25(6)° [83.66(6) to 101.38(6)° in the second independent molecule], the most acute angle in each case being associated with the Pd_2S_2 ring. The Pd−S distances in the four-membered ring are effectively the same at ca. 2.31 Å (Table 1) and the Pd−S bond to S(2), trans to chlorine, is ca. 0.05 Å shorter than that to S(1), trans to sulfur. The pseudo-six-membered chelate ring formed by Pd/S(1)/C(1)/Fe/C(6)/S(2) has a sharply folded conformation with an out-of-plane fold angle about the S(1)···S(2) vector of ca. 71° [73°]; the nonbonded S(1)···S(2) separation is 3.17 Å [3.17 Å] and the transannular Pd···Fe separation is 3.88 Å [3.82 Å]. The ferrocenediyl units in both independent molecules have essentially eclipsed geometries with stagger angles of less than 5°, the rings being nearly parallel (maximum inclination of 2°). The only intermolecular interaction of note is the formation, to each independent complex, of C−H···Cl hydrogen bonds from the ordered included chloroform solvent molecules; the C···Cl and H···Cl distances are 3.45, 2.55 Å [3.52, 2.65 Å] with C−H···Cl angles of 152° [148°]. There are no intercomplex interactions of note.

The ^{1}H NMR shows an extremely broad ferrocenyl region, with a broad singlet for the *tert*-butyl protons. The mass spectrum shows a very small peak for the molecular ion, and fragment peaks for loss of chloride, and for the loss of both chlorides and both *tert*-butyl groups. A peak for the free ligand is also evident. For **5** to be formed, the disulfane, **3**, must first be reduced to the thiolate. The thiolate is unstable and spontaneously oxidizes back to the disulfane in the presence of oxygen. As the reaction was not done under an inert atmospheres (as it was not expected to be air-sensitive) an improved yield would be expected if the reaction were run under nitrogen in degassed solvents. The reducing agent has not been identified, though the square-planar geometry of the metal center shows that the incorporated palladium remains in the +2 oxidation state.

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(8) Gibson, V. C.; Long, N. J.; White, A. J. P.; Williams, C. K.; Williams, D. J. *Chem. Commun.* **2000**, 2359.

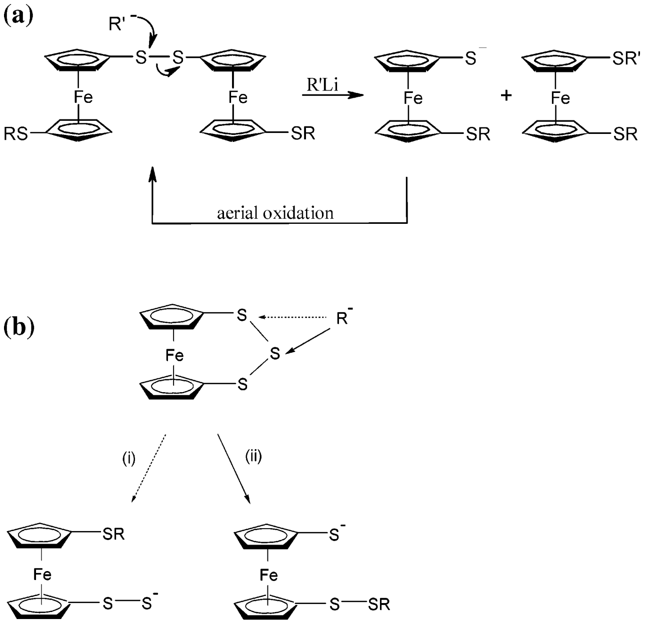

Figure 4. Cleavage of (a) bis(1′-organothiolatoferrocenyl)-disulfanes with organolithiums and (b) 1,2,3-trithia-[3]-ferrocenophane with organolithiums.

III. Cleavage of the Disulfanes To Give 1,1′-Bis-(organylthiolato)ferrocenes: Synthesis. Several unsymmetrical 1,1′-bis(organylthiolato)ferrocenes (FcSMeSPh, **6**; FcS^{t}BuSMe, **7**; FcS^{t}BuSPh, **8**) have been synthesized (Scheme 1). **6** and **7** were isolated as deep orange oils, whereas **8** is a yellow solid. All the species are air-stable and soluble in most common organic solvents, though **8** is only sparingly soluble in alcohols. Three methods (A, B, and C) were utilized and though method **C** did not give pure products, it did allow elucidation of the mechanism for 1,2,3-trithia-[3]-ferrocenophane cleavage, leading to an explanation of the origin of the different products formed during the synthesis of bis(1′-organylthiolatoferrocenyl)disulfanes.

Method A. Organolithium reagents can be used to cleave the disulfide bridge of bis(1′-organothiolatoferrocenyl)disulfanes. This was already shown when methyllithium was used to cleave bis(1′- mesitylthiolatoferrocenyl)disulfide.[8] This methodology has been used to synthesize **6** and **8** by cleaving **1** and **3**, respectively, with phenyllithium. The products are easily purified by column chromatography. **6** was isolated in only a 30% yield as a deep orange oil, and **8** in a 50% yield as a yellow solid (the maximum yield possible as the other 50% reforms the starting material on exposure to air) (Figure 4a).

Method B. Yields can be improved by cleaving the disulfide symmetrically. This allows both of the ferrocenyl units to become 1,1′-disubstituted products, hence giving a maximum yield of 100%. The only limitation is that any aromatic substituents must be introduced first as they cannot easily be introduced by nucleophilic substitution reactions. Both **2** and **3** were cleaved with lithiumtriethylborohydride to give a 1-thiolato,1′-organothiolatoferrocene. These were then used as nucleophiles in substitution reactions with alkyl halides to give **6**−**8** (Scheme 1).

Methyl groups were easily introduced using methyl iodide. When **2** and **3** were cleaved and reacted with methyl iodide **6** and **7** were synthesized in near quantitative yield. Both of these reactions were carried out in THF at room temperature. Attempts were made to introduce *tert*-butyl groups to cleaved **2** by using *tert*-butyl bromide as the alkyl halide to give FcS^{t}BuSPh (**8**), but with only limited success. When THF is used as the solvent there is no reaction even after reflux for 24 h. This is not too surprising as nucleophilic substitutions with *tert*-butyl bromide go via an S_N1 mechanism. S_N1 reactions require polar, protic solvents (such as water or methanol) to proceed efficiently, but such solvents cannot be used in the first step of the reaction as lithium triethylborohydride will reduce with them.

Method C. The "One-Pot" Reaction: Elucidation of the Mechanism for 1,2,3-Trithia-[3]-ferrocenophane Cleavage. Unlike the other methods used for synthesizing 1,1′-bis(organothiolato)-ferrocenes this method did not involve the isolation of a disulfane. As before, 2 equiv of phenyllithium were reacted with 1,2,3-trithia-[3]-ferrocenophane. However, instead of being exposed to the air, and undergoing oxidation, the unstable intermediate (as proposed by Herberhold[9]) was kept under an inert atmosphere and reacted with methyl iodide. It was hoped that FcSPhSMe (**6**) would then be produced, probably in a higher yield than those recorded for the other methods. However, though large amounts of the desired products were formed, this was coupled with significant amounts of BMSF and BPSF that proved to be inseparable by column chromatography (ratio **6** (63%):MSF (33%):BPSF (4%)).

Realistically, the only reaction methyl iodide can partake in is nucleophilic substitution. Therefore, any methylthio groups in the products must have been produced from thiolato attack on methyl iodide. Therefore, the intermediates shown below must all be produced from the cleavage of 1,2,3-trithia-[3]-ferrocenophane with phenyllithium. Now that the products of the cleavage are known the mechanism can be postulated. Attack on the sulfur bridge of 1,2,3-trithia-[3]-ferrocenophane can occur in two places, either on the first sulfur of the bridge, route i, or on the central sulfur, route ii (Figure 4b). The reaction uses 2 equiv of the organolithium; therefore the intermediate produced in the first step must also be susceptible to nucleophilic attack. The intermediate in route (i) can only realistically (a negatively charged lithium reagent is unlikely to attack a negatively charged atom) be attacked at the first sulfur of the disulfide, eliminating S_2^- to give the symmetrical 1,1′-bisorganylthiolatoferrocenyl species. Attack by the second equivalent of the organolithium on the intermediate produced by route ii can occur at either sulfur atom of the disulfide, giving the 1,1′-dithiolato or the 1-thiolato,1′-thioether ferrocenediyl species, eliminating R_2S and RS^-, respectively. The product distribution will vary with different organolithium reagents, based on their reactivity and sterics. For instance, *tert*-butyllithium is much more reactive than phenyllithium and on these grounds would therefore show an increased preference for route i. In contrast, however, *tert*-butyllithium is also more sterically bulky than phenyllithium, which would favor attack at the bridgehead sulfur (route ii).

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[9] Herberhold, M.; Brendel, H. *J. Organomet. Chem.* **1991**, *413*, 65.

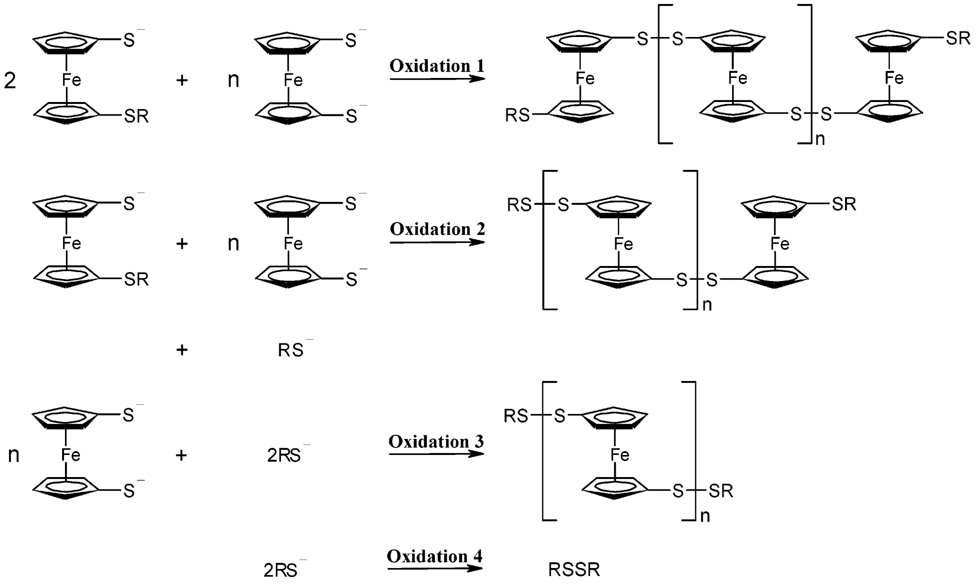

Figure 5. Possible products from the oxidation step of method **4**.

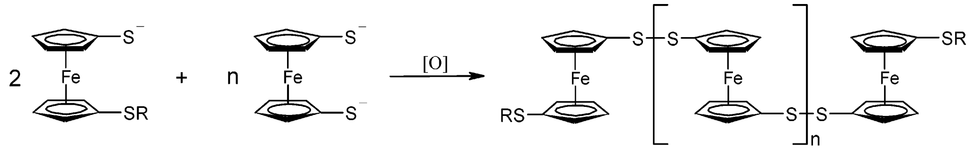

Figure 6. Oxidation step without RS^-.

Via this mechanism, the products produced from aerial oxidation of the reaction mixture can be explained. There are three thiolato species that can oxidize to form disulfides: RS^-, RS-Fc-S^-, and S^--Fc-S^-. As one of them is a dithiolato species it need not be just two species that combine. The combinations are shown in Figure 5. Obviously the larger *n* the more unlikely that combination is. When water is added to the reaction mixture, before the THF is removed, the impurities and the monomeric ferrocenyl species are not observed. The amount of the three thiolato species cannot be affected at this point, but the way in which they oxidize can. If the RS^- species is "removed" from reaction then the range of products is reduced. Monomeric ferrocenyl species cannot be formed as no nonferrocenyl thiolato species are present (Figure 6). The water addition forces RS^- to oxidize with itself to give RSSR (oxidation 4, Figure 5), leaving the ferrocenyl species free to form the products shown above. The oxidation of thiolates by oxygen proceeds via an electron-transfer mechanism, initially giving a thiyl radical and a peroxide ion. Dimerization of the thiyl radical gives the disulfide.

Characterization. As with the bis(1′-organylthiolatoferrocenyl)disulfanes, an AA′BB′CC′DD′ splitting pattern is expected in the ^{1}H NMR, appearing as four pseudotriplets. This pattern is clearly evident for **6**−**8**, although there is significant overlapping in some of the spectra. Precise assignment of the triplets to specific protons is difficult, but tentative assignments can be made by comparison to the analogous symmetrically substituted ferrocenes.[10] All of the pseudotriplets occur downfield of ferrocene (δ 4.04 ppm), indicating that both the alkyl- and aryl-thio substituents are slightly electron withdrawing.

The positive ion FAB mass spectra of all three ligands gave strong molecular ions, with the *tert*-butyl-substituted ligands showing a peak at $[M - 56]^+$ indicating a tendency to lose the *tert*-butyl substituent. **8** also showed a peak for 1-(*tert*-butylthio),1′-(thiolato)ferrocene from unsymmetrical cleavage of the ethyl bridge.

IV. Metal Complexes of Ligands 6−8. Complexes of **6**−**8** have been formed via reaction with palladium(II), platinum(II), and tungsten(0) reagents (Scheme 2).

Preparation of Platinum and Palladium Complexes. The dichloroplatinum and -palladium complexes of **6**−**8** have all been synthesized by reacting a small excess of ligand with $[M(PhCN)_2Cl_2]$ (M = Pt, Pd) in toluene at 60 °C for 20 h. The complexes were isolated as deep-brown solids in yields between 64% and 75%. All of the complexes (**9**−**14**) were insoluble in nonpolar solvents, and most only sparingly soluble in chlorinated solvents. ^{1}H NMR spectra were measured for all of the complexes except for **14**, which was not sufficiently soluble to give a signal, and significant changes occur in the spectra when compared to those for the free ligands. Several broad peaks are observed in the ferrocenyl region, all of which are significantly shifted downfield (some by over 1 ppm). The peaks for the sulfur substituents are also shifted downfield with slight broadening. The downfield shift can be assigned to magnetic anisotropy, or the inductive effect of the metal dihalide moiety. As with other [3]-ferrocenophanes, the broad signals can be attributed to fluxionality. There are two fluxional modes that operate, the first being bridge reversal, which is analogous to the chair−chair conformational exchange observed in cyclohexane. The rate of bridge reversal depends on the length of the

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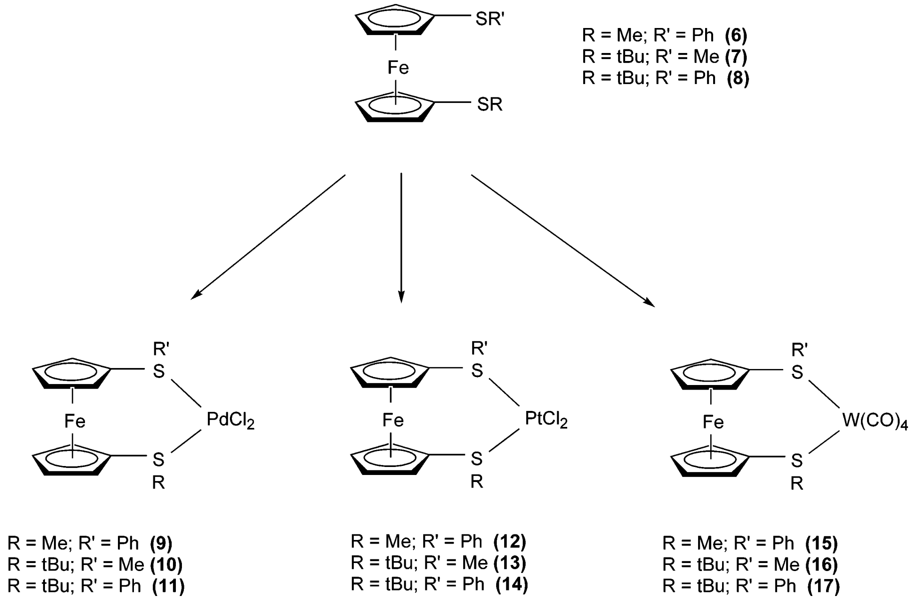
[10] Orrell, K. G.; Sik, V.; Brubaker, C. H., Jr.; McCulloch, B. *J. Organomet. Chem.* **1984**, *276*, 267.

Scheme 2. Formation of Compounds 9−17



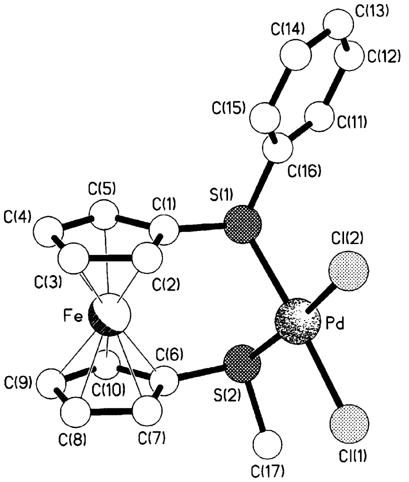


Figure 7. The molecular structure of **9**.

bridge, and the atoms that make up the bridge. The second fluxional mode, which only occurs in heteroatom-substituted ferrocenophanes, is pyramidal heteroatom inversion. In symmetrically substituted 1,1′-bis(organylthiolato)ferrocenes complexed to MX_2 metal fragments (M = Pd, Pt) the rate of sulfur inversion is dependent on the transition metal, the halogen, and the sulfur substituent.[10] Sulfur inversion tends to be slow on the NMR time scale. These fluxional processes in related compounds have been well-studied and we believe similar findings would be observed here but this has not been pursued.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 9

Pd−S(1)	2.3134(13)	Pd−S(2)	2.3225(14)
Pd−Cl(1)	2.294(2)	Pd−Cl(2)	2.299(2)
S(1)−C(1)	1.767(5)	S(2)−C(6)	1.755(6)
Cl(1)−Pd−Cl(2)	90.45(6)	Cl(1)−Pd−S(1)	175.90(6)
Cl(2)−Pd−S(1)	93.59(5)	Cl(1)−Pd−S(2)	93.40(6)
Cl(2)−Pd−S(2)	175.24(5)	S(1)−Pd−S(2)	82.54(5)
C(1)−S(1)−C(16)	104.5(2)	C(1)−S(1)−Pd	103.0(2)
C(16)−S(1)−Pd	114.87(14)	C(6)−S(2)−C(17)	100.3(3)
C(6)−S(2)−Pd	101.6(2)	C(17)−S(2)−Pd	113.7(3)

A two-layer crystallization (dichloromethane:hexane 1:1) of **9** gave orange platy needles suitable for an X-ray diffraction study. The complex has a solid-state structure in which the ferrocenediyl units have an eclipsed geometry (stagger and inclination angles of less than 1°) and a nonbonded S···S contact of 3.06 Å (Figure 7, Table 2). The six-membered chelate ring (vide supra) has a steeply folded geometry very similar to that seen for **5** with an out-of-plane bend about the S(1)···S(2) vector of ca. 76°, the sulfur lone pairs both lying on the same side of the palladium coordination plane; the nonbonded Pd···Fe separation is 3.76 Å. Distortions in the geometry at palladium are small with cis angles in the range 82.54(5)−93.59(5)°. The only intercomplex interaction of note is a parallel $\pi-\pi$ stacking of C_i-related *S*-phenyl rings having mean interplanar and centroid···centroid separations of 3.56 and 4.24 Å, respectively.

Preparation of Tungsten Complexes. $W(CO)_5(thf)$ is a well-known precursor for tungsten complexes and can be made by irradiating a THF solution of tungsten hexacarbonyl with UV radiation (from a mercury lamp, 125 W). With longer irradiation times, significant quantities of $W(CO)_4(thf)_2$ may also be produced. When synthesizing the tungsten complexes of the ferrocenediyl ligands **6**−**8** the tungsten hexacarbonyl solution was irradiated for 10 min, giving significant quantities of both the penta- and tetracarbonyl precursors. The precursor solution was then added to a solution of each of the ligands **6**−**8** in THF and stirred for 20 h at room temperature; however, only 1-(*tert*-butylthio),1′-(methylthio)ferrocene (**7**) reacted well to give **16**. The other two solutions were heated at 40 °C for a further 24 h, which gave small quantities of **17** but no **15** (Scheme 2). It is possible that the phenylthio group is not a strong enough donor to displace a THF ligand (remembering that THF is present in a huge excess as it is the solvent).

The complexes **16** and **17** were characterized by ^1H NMR, IR, and mass spectrometry. In contrast to the platinum and palladium derivatives these complexes show four sharp pseudotriplets in their ^1H NMR. This indicates that both the fluxional processes (bridge reversal and sulfur inversion) are at their fast-exchange

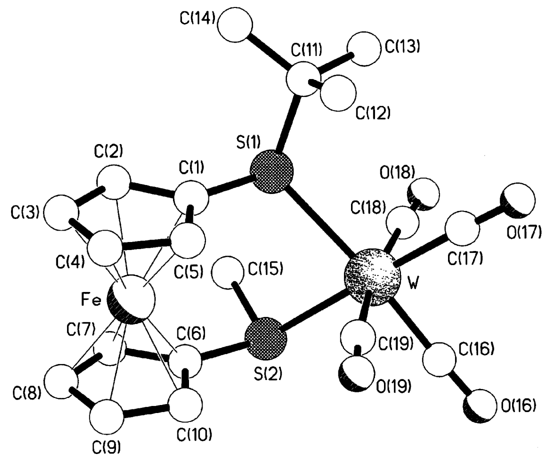


Figure 8. The molecular structure of **16**.

limit. All four have significant downfield shifts from the free ligand and as expected there are also downfield shifts of the pendant thioether groups. The mass spectra of **16** and **17** show the molecular ion and a sequence of peaks from the loss of carbon monoxide and *tert*-butyl (which weighs approximately the same as two carbon monoxides). Tungsten fragments are easily identified from their isotope pattern ($^{180}\mathrm{W} = 0.13\%$, $^{182}\mathrm{W} = 26.3\%$, $^{183}\mathrm{W} = 14.3\%$, $^{184}\mathrm{W} = 30.6\%$, $^{186}\mathrm{W} = 28.6\%$). The CO stretches in the IR spectra for **16** and **17** match the pattern for symmetrically substituted ferrocenediyl tungsten complexes,[11] indicating that the asymmetry of the ligand is too far away to significantly affect the carbonyl stretches.

Crystals of **16** suitable for X-ray structure determination were grown by cooling a dichloromethane–hexane (1:1) solution to 0 °C. An X-ray analysis shows **16** to have a structure very similar to that of its PPh_2,SMe analogue[6b] but with the sulfur lone pairs lying on opposite sides of the equatorial tungsten coordination plane (Figure 8), cf. the syn geometries observed in **5** and **9**. This anti relationship of the lone pairs in **16** is a consequence of an inversion of the chirality at one of the sulfur centers. The six-membered chelate ring has a ca. 55° fold about the S(1)···S(2) vector and the C_5H_4 rings are eclipsed (stagger of 2°) and essentially parallel (tilt of 2°). The nonbonded W···Fe distance is 4.37 Å, cf. 4.36 Å in the PPh_2,SMe analogue.[6b] Distortions from octahedral geometry at tungsten are small with cis angles ranging between 86.4(3)° and 99.6(2)°. The axial W–CO bond lengths are both essentially the same (Table 3) and are noticeably slightly longer (by ca. 0.07 Å) than their equatorial counterparts. There are no noteworthy intermolecular packing interactions.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 16

W–S(1)	2.585(2)	W–S(2)	2.565(2)
W–C(16)	1.964(8)	W–C(17)	1.970(8)
W–C(18)	2.026(7)	W–C(19)	2.043(7)
S(1)–C(1)	1.755(7)	S(2)–C(6)	1.769(7)
C(16)–W–C(17)	87.9(3)	C(16)–W–C(18)	87.7(3)
C(17)–W–C(18)	86.4(3)	C(16)–W–C(19)	87.2(3)
C(17)–W–C(19)	86.4(3)	C(18)–W–C(19)	171.3(3)
C(16)–W–S(2)	89.8(2)	C(17)–W–S(2)	176.2(2)
C(18)–W–S(2)	90.5(2)	C(19)–W–S(2)	96.4(2)
C(16)–W–S(1)	171.3(2)	C(17)–W–S(1)	99.6(2)
C(18)–W–S(1)	88.3(2)	C(19)–W–S(1)	97.7(2)
S(2)–W–S(1)	82.59(5)	C(1)–S(1)–C(11)	102.1(3)
C(1)–S(1)–W	114.7(2)	C(11)–S(1)–W	117.0(2)
C(6)–S(2)–C(15)	100.3(3)	C(6)–S(2)–W	113.8(2)
C(15)–S(2)–W	109.7(2)		

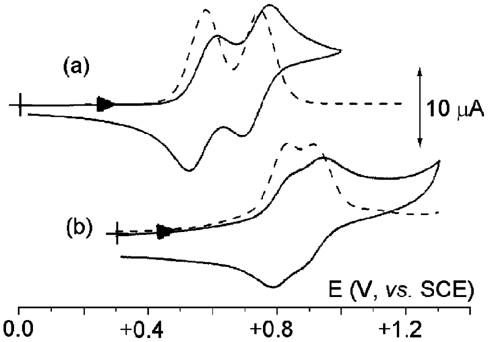


Figure 9. Cyclic (—) and Osteryoung square wave (- - -) voltammograms recorded at a platinum electrode in CH_2Cl_2 solutions containing (a) **3** (1.0×10^{-3} mol dm^{-3}) and (b) **5** (0.8×10^{-3} mol dm^{-3}). Supporting electrolyte: $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) Scan rates: (—) 0.2 V s^{-1}; (- - -) 0.1 V s^{-1}.

Electrochemistry. As previously reported for unsubstituted diferrocenyldisulfane,[12] complexes **1** and **3** in CH_2Cl_2 solution exhibit two separated one-electron oxidations. As a typical example, Figure 9a shows the cyclic voltammetric profile of complex **3**. Also illustrated is the voltammetric response of the dipalladium complex **5**, Figure 9b, which originates from complex **3** (see above). It is noted that, despite the features of chemical reversibility of the sequence [**3**]/[**3**]$^+$/[**3**]$^{2+}$, step-by-step controlled electrolysis followed by cyclic voltammetric tests on the resulting solutions proved that the monocation [**3**]$^+$ is quite stable, whereas the dication [**3**]$^{2+}$ slowly decomposes. On passing from **3** to [**3**]$^+$, the original yellow solution turns orange-brown, thus suggesting that the sulfur substituents significantly contribute to the HOMO level of the mixed-valent ferrocenium monocation (iron-centered ferrocenium species are blue to green).

In qualitative terms, similar behavior is displayed by complex **1**. Both complexes also exhibit a further irreversible oxidation at higher potential values (E_p in the range +1.5 to +1.6 V), which is attributed to the disulfane bridge. Complex **5** also exhibits two separated one-electron oxidations, even if their separation ($\Delta E°'$ = 85 mV) is significantly lower than that of complexes **3** and **1** ($\Delta E°'$ = 150 mV), presumably due to the increased distance between the iron centers. The closeness of the two steps prevented the determination of the stability of the monocation [**5**]$^+$ by controlled potential coulometry, but also in this case exhaustive two-electron oxidation led to decomposition. Though not shown in the figure, complex **5** also undergoes a single irreversible reduction, ($E_p = -1.0$ V), which is designated as palladium-centered.

Since the separation between the formal electrode potentials of two redox sites present in a molecule is routinely assumed to be representative of the degree of their intramolecular electronic communication,[13] it is suggested that the electronic mobility in **3** (and **1**) is

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Table 4. Formal Electrode Potentials (V vs SCE) and Peak-to-Peak Separations (mV) for the Ferrocene-Centered Processes Exhibited by Complexes 1, 3, and 5 in CH_2Cl_2 Solution

complex	$E°'_{0/+}$	$\Delta E_p{}^a$	$E°'_{+/2+}$	$\Delta E_p{}^a$
1	+0.50	60	+0.65	65
3	+0.59	62	+0.74	71
5	+0.83[b]	*c*	+0.92	*c*
FcH	+0.39	60		

[a] Measured at 0.1 V s^{-1}. [b] From OSWV. [c] Difficult to measure.

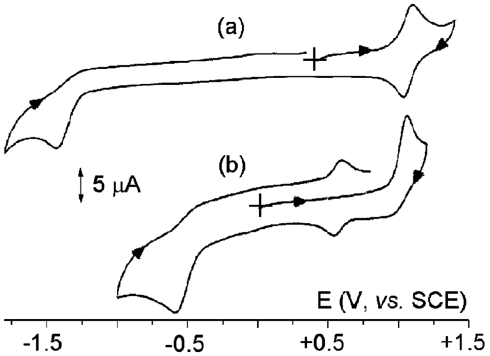

Figure 10. Cyclic voltammograms recorded at a platinum electrode in CH_2Cl_2 solutions containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) and (a) **12** (0.8×10^{-3} mol dm^{-3}) or (b) **9** (0.9×10^{-3} mol dm^{-3}). Scan rate: 0.2 V s^{-1}.

higher than that in **5**. It is, however, important to underline that in **5** the insertion of the two palladium atoms does not compromise the mutual interaction between the two peripheral ferrocenediyl units.

From the electrochemical viewpoint, based on the respective comproportionation constants[13] ($[\mathbf{1}]^+$, $K_{com} = 340$; $[\mathbf{3}]^+$, $K_{com} = 340$; $[\mathbf{5}]^+$, $K_{com} = 26$), the mixed-valent monocations $[\mathbf{1}]^+$ and $[\mathbf{3}]^+$ belong to the partially delocalized Robin-Day Class II, whereas $[\mathbf{5}]^+$ belongs to the localized Class I.[14] The formal electrode potentials of the redox processes of complexes **1**, **3**, and **5** are reported in Table 4.

The difference in redox potentials between **1** and **3** is obviously expected on the basis of the inductive effects of the substituents, and as expected the complexation of **3** with palladium makes the oxidation significantly more difficult. Considering the metalloferrocenophanes **9**−**14**, as a representative example, Figure 10 compares the cyclic voltammetric profile of the platinum complex **12** with that of the corresponding palladium complex **9**. As already observed for related complexes[15] (and in contrast to the platinum complexes that afford an oxidation process with features of transient chemical reversibility in the cyclic voltammetric time scale), the palladium complexes give rise to an oxidation process that is accompanied by fast release of the corresponding free ferrocene ligands. It is, however, noted that in the long times of macroelectrolysis, the electrogenerated platinum monocations tend to decompose. All the platinum and palladium complexes also show the irreversible reduction assigned to the M(II)/M(0) electron transfer. The pertinent electrochemical data are compiled in Table 5.

Table 5. Formal Electrode Potentials (V vs SCE) and Peak-to-Peak Separations (mV) for the Redox Processes Exhibited by Complexes 9−14 in CH_2Cl_2 Solution

complex	$E°'_{(0/+)}$	$\Delta E_p{}^a$	$i_{pc}/i_{pa}{}^b$	$E_{p(0/2-)}{}^a$
9 (Pd)	+1.08[c,a]			−0.67
10 (Pd)	+1.04	60	0.3	−0.60
11 (Pd)	+1.05[c,a]			−0.58
12 (Pt)	+1.08	60	0.7	−1.43
13 (Pt)	+1.00	62	0.7	−1.64
14 (Pt)	+0.99	80	0.5	−1.34

[a] Measured at 0.1 V s^{-1}. [b] Measured at 0.2 V s^{-1}. [c] Peak potential value for irreversible processes.

Experimental Section

General Procedures. All preparations were carried out with the standard Schlenk techniques.[16] All solvents were distilled over standard drying agents under nitrogen directly before use and all reactions were carried out under an atmosphere of nitrogen. Alumina gel (neutral, grade II) was used for chromatographic separations. All NMR spectra were recorded with use of a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 250.1 MHz (^1H). Chemical shifts are reported in δ with $CDCl_3$ (^1H, δ 7.25 ppm) as the reference for the spectra. Infrared spectra were recorded with NaCl solution cells (CH_2Cl_2) and a Mattson Polaris Fourier Transform IR spectrometer. Mass spectra were recorded by using positive FAB methods, on an Autospec Q mass spectrometer. Microanalyses were carried out in the Department of Chemistry, University of North London.

Starting Materials. 1,2,3-Trithia-[3]-ferrocenophane,[17] $[Pd(PhCN)_2Cl_2]$,[18] $[Pt(PhCN)_2Cl_2]$,[18] and $[Cu(MeCN)_4]PF_6$[19] were synthesized by using standard literature procedures, except that the 1,1′-dilithioferrocene intermediate in the synthesis of 1,2,3-trithia-[3]-ferrocenophane was used in situ. All chemicals were purchased from Aldrich, except for ^{t}BuLi, MeLi, and $LiEt_3BH$, which were purchased from Acros.

Preparation of Bis(1′-organylthiolatoferrocenyl)disulfanes. General procedure: To a solution of 1,2,3-trithia-[3]-ferrocenophane (1 equiv) in dry deoxygenated THF cooled to −78 °C was added an organolithium reagent (2.2 equiv). The orange solution gradually darkened to deep red on warming to room temperature and stirring for 20 h. The reaction was exposed to the air and water was added (50 mL). The THF was removed under vacuum and the aqueous layer extracted with dichloromethane (8×50 mL). The combined organic fractions were dried ($MgSO_4$) and evaporated to dryness. Column chromatography (7:3 hexane:dichloromethane) allowed the separation of the products. All of the columns gave small amounts of 1,2,3-trithia-[3]-ferrocenophane, and several other yellow fractions. The first of which was the desired product.

Bis(1′-methylthiolatoferrocenyl)disulfane (1): Reaction of 1,2,3-trithia-[3]-ferrocenophane (1.40 g, 5.00 mmol) with MeLi (1.6 M in ether, 7.0 mL, 11.2 mmol) gave an oily orange crude product. Column chromatography (7:3 hexane:dichloromethane) gave MeS-Fc-SS-Fc-SMe (0.53 g, 1.00 mmol, 40%

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yield) as a deep-red oil. Anal. Calcd for $C_{22}H_{22}S_4Fe_2$: C, 50.20, H, 4.21. Found: C, 50.26, H, 4.25. ^{1}H NMR ($CDCl_3$, 270 MHz, ppm) δ 4.30−4.25 (m, 12H, C_5H_4), 4.15 (t, 4H, C_5H_4), 2.25 (s, 6H, CH_3). Mass spectrum (*m*/*z*): 526 ([M]$^+$), 263 ([M − SfcSMe]$^+$). Crystals suitable for X-ray analysis were grown from slow evaporation of a hexane solution. Crystal data for **1**: $C_{22}H_{22}S_4Fe_2$, $M = 526.3$, orthorhombic, $Pna2_1$ (no. 33), $a = 14.820(1)$ Å, $b = 6.271(1)$ Å, $c = 23.169(1)$ Å, $V = 2153.2(2)$ Å^3, $Z = 4$, $D_c = 1.624$ g cm^{-3}, μ(Cu Kα) = 14.5 mm^{-1}, $T = 293$ K, yellow platy needles; 1524 independent measured reflections, F^2 refinement, $R_1 = 0.052$, $wR_2 = 0.132$, 1374 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$], 255 parameters. Polarity tests gave evidence of racemic twinning [$R_1{}^+ = 0.0573$, $R_{1-} = 0.0581$, $x^+ = +0.51(3)$, $x- = +0.49(3)$] and no absolute structure could be assigned. CCDC 229586.

Bis(1′-phenylthiolatoferrocenyl)disulfane (2): Reaction of 1,2,3-trithia-[3]-ferrocenophane (2.01 g, 7.14 mmol) with PhLi (1.8 M in cyclohexane/ether (7:3), 9.0 mL, 16.20 mmol) gave an oily orange crude product. Column chromatography (7:3 hexane:dichloromethane) gave PhS-Fc-SS-Fc-SPh as a yellow powder (0.58 g, 0.90 mmol, 25% yield) and the trimeric species PhS-Fc-SS-Fc-SS-Fc-SPh (**4**) (0.12 g, 0.13 mmol, 5% yield) also as a yellow powder. PhS-Fc-SS-Fc-SPh (**2**): Anal. Calcd for $C_{32}H_{26}S_4Fe_2$: C, 59.09, H, 4.03. Found: C, 59.14, H, 3.94. ^{1}H NMR ($CDCl_3$, 270 MHz, ppm) δ 7.18−7.11 (m, 2H, C_6H_5), 7.07−6.99 (m, 3H, C_6H_5), 4.39−4.37 (m, 6H, C_5H_4), 4.32 (t, 2H, C_5H_4). Mass spectrum (*m*/*z*): 650 ([M]$^+$), 325 ([M − SFcSPh]$^+$). PhS-Fc-SS-Fc-SS-Fc-SPh (**4**): Anal. Calcd for $C_{42}H_{34}S_6Fe_3$: C, 56.14, H, 3.81. Found: C, 56.21, H, 3.75. ^{1}H NMR ($CDCl_3$, 270 MHz, ppm) δ 7.17−7.12 (m, 4H, C_6H_5), 7.06−6.98 (m, 6H, C_6H_5), 4.38−4.21 (m, 24H, C_5H_4). Mass spectrum (*m*/*z*): 898 ([M]$^+$), 325 ([PhSFcS]$^+$).

Bis(1′-*tert*-butylthiolatoferrocenyl)disulfane (3): Reaction of 1,2,3-trithia-[3]-ferrocenophane (3.06 g, 10.92 mmol) with ^{t}BuLi (1.5 M in pentanes, 16.0 mL, 24.00 mmol) gave an orange crude product. Column chromatography (7:3 hexane: dichloromethane) gave ^{t}BuS-Fc-SS-Fc-S^{t}Bu (2.33 g, 3.81 mmol, 70% yield) as a flaky, semicrystalline yellow solid. Anal. Calcd for $C_{28}H_{34}S_4Fe_2$: C, 55.09, H, 5.61. Found: C, 55.48, H, 5.27. ^{1}H NMR ($CDCl_3$, 270 MHz, ppm) δ 4.28 (s, 8H, C_5H_4), 4.26 (t, 4H, C_5H_4), 4.20 (t, 4H, $^3J = 1.7$ Hz, C_5H_4), 1.14 (s, 18H, CH_3). Mass spectrum (*m*/*z*): 610 ([M]$^+$), 305 (([M − SFcS^{t}Bu]$^+$)), 249 ([S − Fc − S]$^+$).

Preparation of Bis(1′-*tert*-butylthiolatoferrocenyl)-disulfane Complex of Palladium (5). General procedure: To a solution of [M(PhCN)$_2$Cl$_2$] (M = Pt, Pd) (1 equiv) in toluene (50 mL) at 60 °C was added a toluene (10 mL) solution of the ligand (**3**) (1.1 equiv). The solution immediately darkened and was stirred for 20 h by which time a dark precipitate had formed. The reaction was cooled and the precipitate filtered, washed with hot hexane (50 mL) and diethyl ether (50 mL), and dried in vacuo for 1 h, to give a dark-red precipitate of [{FcS^{t}Bu(μ-S)}$_2$Pd$_2$Cl$_2$] (0.03 g, 0.04 mmol, 28% yield). Anal. Calcd for $C_{28}H_{34}S_4Fe_2Pd_2Cl_2$: C, 37.61, H, 3.83. Found: C, 38.07, H, 3.76. ^{1}H NMR ($C_2D_2Cl_2$, 270 MHz, ppm) δ 5.10−4.00 (m, br, 16H, C_5H_4), 1.36 (s, 18H, CH_3). Mass spectrum (*m*/*z*): 894 ([M]$^+$), 857 ([M − Cl]$^+$), 709 ([M − 2Cl − ^{t}Bu]$^+$), 305 ([FcS^{t}BuS]$^+$). Crystals suitable for X-ray diffraction were grown by slow evaporation of a $CHCl_3$ solution. Crystal data for **5**: $C_{28}H_{34}S_4Cl_2Fe_2Pd_2\cdot 2CHCl_3$, $M = 1132.9$, triclinic, $P\bar{1}$ (no. 2), $a = 11.441(1)$ Å, $b = 13.605(1)$ Å, $c = 13.961(1)$ Å, $\alpha = 89.41(1)°$, $\beta = 72.57(1)°$, $\gamma = 79.37(1)°$, $V = 2035.4(3)$ Å^3, $Z = 2$ (two independent C_i symmetric molecules), $D_c = 1.849$ g cm^{-3}, μ(Mo Kα) = 2.32 mm^{-1}, $T = 293$ K, very dark-brown needles; 7167 independent measured reflections, F^2 refinement, $R_1 = 0.046$, $wR_2 = 0.093$, 5049 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 416 parameters. CCDC 229587.

Cleavage of the Disulfides To Give 1,1′-Bis(organylthiolato)ferrocenes, FcSRSR′. Method A. General procedure: To a solution of the bis(1′-organylthiolatoferrocenyl)disulfane (1 equiv) in dry deoxygenated THF cooled to −78 °C was added an organolithium reagent (2.2 equiv). The yellow solution was allowed to warm to room temperature and was stirred for 20 h. The reaction was exposed to the air and the solvent removed. The residual orange oil was dissolved in dichloromethane and extracted with water (50 mL). The aqueous layer was further extracted with dichloromethane (5 × 50 mL) and the combined organic fractions dried ($MgSO_4$) and evaporated to dryness. Column chromatography (7:3 hexane:dichloromethane) allowed the separation of the products with the desired product comprising the first band and the starting material the second.

1-(Methylthiolato),1′-(phenylthiolato)ferrocene (6): Reaction of MeS-Fc-SS-Fc-SMe (**1**) (0.20 g, 0.38 mmol) with PhLi (1.8 M in cyclohexane/ether (7:3), 0.5 mL, 0.90 mmol) gave an oily orange crude product. Column chromatography (7:3 hexane:dichloromethane) gave MeS-Fc-SS-Fc-SMe (**6**) (0.13 g, 0.25 mmol) and an orange oil of FcSMeSPh (0.08 g, 0.23 mmol, 30% yield). Anal. Calcd for $C_{17}H_{16}S_2Fe$: C, 60.10, H, 4.74. Found: C, 60.14, H, 4.81. ^{1}H NMR ($CDCl_3$, 270 MHz, ppm) δ 7.19−7.13 (m, 2H, C_6H_5), 7.06−7.02 (m, 3H, C_6H_5), 4.50−4.36 (m, 6H, C_5H_4), 4.27 (t, 2H, C_5H_4), 2.32 (s, 3H, CH_3). Mass spectrum (*m*/*z*): 340 ([M]$^+$).

1-(*tert*-Butylthiolato),1′-(phenylthiolato)ferrocene (8): Reaction of ^{t}BuS-Fc-SS-Fc-S^{t}Bu (**3**) (0.86 g, 1.40 mmol) with PhLi (1.8 M in cyclohexane/ether, 1.75 mL, 3.15 mmol) gave an oily orange crude product. Column chromatography (7:3 hexane:dichloromethane) gave ^{t}BuS-Fc-SS-Fc-S^{t}Bu and FcS^{t}BuSPh (**8**) (0.27 g, 0.71 mmol, 50% yield) as a yellow powder. Anal. Calcd for $C_{20}H_{22}S_2Fe$: C, 61.62, H, 5.99. Found: C, 61.72, H, 5.85. ^{1}H NMR ($CDCl_3$, 270 MHz, ppm) δ 7.18−7.12 (m, 2H, C_6H_5), 7.09−7.00 (m, 3H, C_6H_5), 4.40 (t, 2H, C_5H_4), 4.37 (t, 2H, C_5H_4), 4.36 (t, 2H, C_5H_4), 4.33 (t, 2H, C_5H_4), 1.20 (s, 9H, CH_3). Mass spectrum (*m*/*z*): 382 ([M]$^+$), 326 ([M − ^{t}Bu]$^+$).

Method B. 1-(Methylthiolato),1′-(phenylthiolato)ferrocene (6): To a solution of the bis(1′-phenylthiolatoferrocenyl)disulfane (0.35 g, 0.54 mmol, 1 equiv) in dry deoxygenated THF (40 mL) was added lithium triethylborohydride (1.0 M in THF, 1.35 mL, 1.35 mmol, 2.5 equiv). The solution was stirred for 3 h, during which time the yellow solution turned orange. A deoxygenated solution of methyl iodide (0.15 mL, 2.41 mmol) in THF (20 mL) was added and the reaction was stirred for 20 h. The THF was evaporated to dryness and the crude product redissolved in dichloromethane (50 mL) and washed with water (50 mL) with the aqueous layer being washed further with dichloromethane (3 × 30 mL). The combined organic fractions were dried ($MgSO_4$) and evaporated to dryness. A short column (7:3 hexane:dichloromethane) was run to remove any traces of the starting material to leave an orange oil of FcSMeSPh (0.35 g, 1.01 mmol, 94% yield).

1-(*tert*-Butylthiolato),1′-(methylthiolato)ferrocene (7): To a solution of bis(1′-*tert*-butylthiolatoferrocenyl)disulfane (0.61 g, 1.00 mmol, 1 equiv) in dry deoxygenated THF (50 mL) was added lithium triethylborohydride (1.0 M in THF, 2.50 mL, 2.50 mmol, 2.5 equiv). The solution was stirred for 3 h, during which time the yellow solution turned orange indicating the presence of a ferrocenyl thiolate. A deoxygenated solution of methyl iodide (0.30 mL, 4.82 mmol) in THF (20 mL) was added and the reaction was stirred for 20 h. The THF was evaporated to dryness and the crude product redissolved in dichloromethane (50 mL) and washed with water (50 mL), the aqueous layer being washed further with dichloromethane (3 × 50 mL). The combined organic fractions were dried ($MgSO_4$) and evaporated to dryness. A short column (7:3 hexane: dichloromethane) was run to remove any traces of the starting material giving an orange oil of FcS^{t}BuSMe (0.63 g, 1.98 mmol, 99% yield). Anal. Calcd for $C_{15}H_{20}S_2Fe$: C, 56.25, H, 6.29. Found: C, 56.34, H, 6.41. ^{1}H NMR ($CDCl_3$, 270 MHz, ppm) δ 4.30−4.28 (m, 4H, C_5H_4), 4.25 (vt, 2H, C_5H_4), 4.19 (vt, 2H,

C_5H_4), 2.28 (s, 3H, CH_3), 1.18 (s, 9H, CH_3). Mass spectrum (*m*/*z*): 320 ($[M]^+$), 264 ($[M - {}^tBu]^+$).

Method C. One-Pot Synthesis of 1-Methylthio-1′-phenylthioferrocene, Fc(SMe)(SPh) (6). Excess MeI: To a solution of 1,2,3-trithia-[3]-ferrocenophane (1.26 g, 4.50 mmol) in dry deoxygenated THF (80 mL) at −78°C was added PhLi (1.8 M solution in cyclohexane/ether (7:3), 6.5 mL, 11.7 mmol, 2.6 equiv). The solution was allowed to warm to room temperature and was stirred for 20 h, during which time the orange solution turned deep red. A solution of deoxygenated MeI (3 mL, 48.20 mmol) in dry deoxygenated THF (20 mL) was added, immediately changing to a yellow solution, which was then stirred for 20 h, and the THF was removed in vacuo. The crude product was redissolved in dichloromethane (50 mL) and washed with water (50 mL), the aqueous layer being washed further with dichloromethane (3 × 50 mL). The combined organic fractions were dried ($MgSO_4$) and evaporated to dryness. Column chromatography (9:1 hexane:dichloromethane) gave a deep orange oil (1.28 g) as the first product from the column. The oil was found to contain Fc(SMe)(SPh) (**6**), 1,1′-bis(methylthio)ferrocene (BMSF), and 1,1′-bis(phenylthio)ferrocene (BPSF) in a ratio of approximately 63%:33%: 4% by ^1H NMR integration.

Metal Complexes. Palladium(II) and platinum(II) Complexes. General procedure: To a solution of $[M(PhCN)_2Cl_2]$ (M = Pt, Pd) (1 equiv) in toluene (50 mL) at 60 °C was added a toluene (10 mL) solution of the ligand (FcSRSR′) (1.1 equiv). The solution immediately darkened and was stirred for 20 h by which time a dark precipitate had formed. The reaction was cooled and the precipitate filtered, washed with hot hexane (50 mL) and diethyl ether (50 mL), and dried in vacuo for 1 h to give $[M(FcSRSR')Cl_2]$.

[1-(Methylthiolato),1′-(phenylthiolato)ferrocene]palladium dichloride (9): Reaction of **6** (0.10 g, 0.29 mmol) with bis(benzonitrile)palladium dichloride (0.08 g, 0.25 mmol) gave a dark-brown precipitate of $[Pd(FcSMeSPh)Cl_2]$ (**9**) (0.09 g, 0.18 mmol, 72% yield). Anal. Calcd for $C_{17}H_{16}S_2FePdCl_2$: C, 39.45, H, 3.12. Found: C, 39.40, H, 3.02. ^1H NMR ($C_2D_2Cl_2$, 270 MHz, ppm) δ 7.41−7.30 (m, 3H, C_6H_5), 7.27−7.24 (m, 2H, C_6H_5), 5.30 (br, C_5H_4), 4.57−4.48 (m, br, C_5H_4) (5.30−4.48 ppm = 8H), 2.47 (s, 3H, CH_3). Mass spectrum (*m*/*z*): 518 ($[M]^+$), 483 ($[M - Cl]^+$), 447 ($[M - 2Cl]^+$), 340 ($[FcSMeSPh]^+$). Crystals suitable for X-ray diffraction were grown from a two-layer $C_2H_2Cl_2$−hexane (1:1) solvent system. Crystal data for **9**: $C_{17}H_{16}S_2Cl_2FePd$, M = 517.6, triclinic, $P\bar{1}$ (no. 2), a = 5.872(1) Å, b = 8.669(1) Å, c = 17.882(2) Å, α = 91.82(1)°, β = 94.21(1)°, γ = 102.01(1)°, V = 886.9(2) Å^3, Z = 2, D_c = 1.938 g cm^{-3}, μ(Cu Kα) = 19.7 mm^{-1}, T = 293 K, orange platy needles; 2638 independent measured reflections, F^2 refinement, $R_1 = 0.036$, $wR_2 = 0.084$, 2208 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 120°], 197 parameters. CCDC 229588.

[1-(*tert*-Butylthiolato),1′-(methylthiolato)ferrocene]palladium dichloride (10): Reaction of **7** (0.06 g, 0.20 mmol) with bis(benzonitrile)palladium dichloride (0.07 g, 0.17 mmol) gave a dark-brown precipitate of $[Pd(FcS^tBuSMe)Cl_2]$ (0.05 g, 0.11 mmol, 64% yield). Anal. Calcd for $C_{15}H_{20}S_2FePdCl_2$: C, 36.21, H, 4.05. Found: C, 37.10, H, 4.28. ^1H NMR ($CDCl_3$, 270 MHz, ppm) δ 5.67 (br, C_5H_4), 4.82 (br, C_5H_4), 4.59 (br, C_5H_4), 4.33 (br, C_5H_4) (5.67−4.33 ppm = 8H), 2.45 (s, 3H, CH_3), 1.47 (s, 9H, CH_3). Mass spectrum (*m*/*z*): 498 ($[M]^+$), 463 ($[M - Cl]^+$), 428 ($[M - 2Cl]^+$), 404 ($[M - Cl - {}^tBu]^+$), 371 ($[M - 2Cl - {}^tBu]^+$), 320 ($[FcS^tBuSMe]^+$).

[1-(*tert*-Butylthiolato),1′-(phenylthiolato)ferrocene]palladium dichloride (11): Reaction of **8** (0.06 g, 0.15 mmol) with bis(benzonitrile)palladium dichloride (0.05 g, 0.13 mmol) gave a dark-brown precipitate of $[Pd(FcS^tBuSPh)Cl_2]$ (0.05 g, 0.09 mmol, 67% yield). Anal. Calcd for $C_{20}H_{22}S_2FePdCl_2$: C, 42.92, H, 3.96. Found: C, 42.82, H, 3.87. ^1H NMR ($C_2D_2Cl_2$, 270 MHz, ppm) δ 7.40−7.32 (m, 3H, C_6H_5), 7.25−7.23 (m, 2H, C_6H_5), 5.30 (br, C_5H_4), 4.60 (br, C_5H_4), 4.54 (br, C_5H_4) (5.30−4.54 ppm = 8H), 1.48 (s, 9H, CH_3). Mass spectrum (*m*/*z*): 560 ($[M]^+$), 523 ($[M - Cl]^+$), 488 ($[M - 2Cl]^+$), 467 ($[M - Cl - {}^tBu]^+$), 431 ($[M - 2Cl - {}^tBu]^+$), 382 ($[FcS^tBuSPh]^+$).

[1-(Methylthiolato),1′-(phenylthiolato)ferrocene]platinum dichloride (12): Reaction of **6** (0.10 g, 0.29 mmol) with bis(benzonitrile)platinum dichloride (0.12 g, 0.25 mmol) gave a dark-brown precipitate of $[Pt(FcSMeSPh)Cl_2]$ (0.11 g, 0.19 mmol, 75% yield). Anal. Calcd for $C_{17}H_{16}S_2FePtCl_2$: C, 33.68, H, 2.66. Found: C, 33.58, H, 2.63. ^1H NMR ($C_2D_2Cl_2$, 270 MHz, ppm) δ 7.38−7.32 (m, 8H, C_6H_5), 5.54 (br, C_5H_4), 5.33 (br, C_5H_4), 4.92 (br, C_5H_4), 4.71 (br, C_5H_4), 4.61 (br, C_5H_4), 4.44 (br, C_5H_4), 4.35 (br, C_5H_4), (5.54−4.35 ppm = 8H), 2.63 (s, 3H, $^3J_{Pt-H}$ = 43.3 Hz; CH_3). Mass spectrum (*m*/*z*): 606 ($[M]^+$), 571 ($[M - Cl]^+$), 340 ($[FcSMeSPh]^+$).

[1-(*tert*-Butylthiolato),1′-(methylthiolato)ferrocene]platinum dichloride (13): Reaction of **7** (0.93 g, 0.29 mmol) with bis(benzonitrile)platinum dichloride (0.12 g, 0.25 mmol) gave a dark-brown precipitate of $[Pt(FcS^tBuSMe)Cl_2]$ (0.10 g, 0.18 mmol, 70% yield). Anal. Calcd for $C_{15}H_{20}S_2FePtCl_2$: C, 30.73, H, 3.44. Found: C, 30.75, H, 3.18. ^1H NMR ($C_2D_2Cl_2$, 270 MHz, ppm) δ 4.85−435 (m, br, 8H, C_5H_4), 2.50 (s, 3H, CH_3), 1.48 (s, 9H, CH_3). Mass spectrum (*m*/*z*): 320 (FcS^tBuSMe).

[1-(*tert*-Butylthiolato),1′-(phenylthiolato)ferrocene]platinum dichloride (14): Reaction of **8** (0.05 g, 0.13 mmol) with bis(benzonitrile)platinum dichloride (0.05 g, 0.11 mmol) gave a dark-brown precipitate of $[Pt(FcS^tBuSPh)Cl_2]$ (0.06 g, 0.09 mmol, 68% yield). Anal. Calcd for $C_{20}H_{22}S_2FePtCl_2$: C, 37.03, H, 3.39. Found: C, 37.33, H, 3.25. ^1H NMR ($C_2D_2Cl_2$, 270 MHz, ppm): too insoluble to get a signal.

Tungsten(0) Complexes. Preparation of W precursor: A solution of tungsten hexacarbonyl was dissolved in dry, degassed THF (200 mL) and irradiated with a mercury UV lamp (125 W, λ = 354 nm, 10 min) to give a sufficiently high concentration of $W(CO)_5thf/W(CO)_4thf_2$. IR/cm^{-1} (THF solution): major signals 1974.1 ($W(CO)_6$), 1927.0 ($W(CO)_5thf$), 1891.5 ($W(CO)_4thf_2$).

[1-(*tert*-Butylthiolato),1′-(methylthiolato)ferrocene]tungsten tetracarbonyl (16): To a solution of **7** (0.10 g, 0.30 mmol, 1 equiv) in dry deoxygenated THF (15 mL) was added to tungsten precursor solution (30 mL, 1.5 equiv (initial concentration: 0.015 mol dm^{-3} $W(CO)_6$ in THF)). The reaction was stirred at room temperature for 20 h and the solvent removed in vacuo. Column chromatography (7:3 hexane: dichloromethane) enabled separation of the product from unreacted ligand to give $[(FcS^tBuSMe)W(CO)_4]$ (**16**) (0.07 g, 0.12 mmol, 40% yield). Anal. Calcd for $C_{19}H_{20}S_2FeW$: C, 37.04, H, 3.27. Found: C, 36.96, H, 3.18. ^1H NMR ($CDCl_3$, 270 MHz, ppm) δ 4.64 (t, 2H, C_5H_4), 4.61 (t, 2H, C_5H_4), 4.36 (t, 2H, C_5H_4), 4.33 (t, 2H, C_5H_4), 2.83 (s, 3H, CH_3), 1.34 (s, 9H, CH_3). Mass spectrum (*m*/*z*): 616 ($[M]^+$), 589 ($[M - CO]^+$), 560 ($[M - {}^tBu]^+$, $[M - 2CO]^+$), 532 ($[M - {}^tBu - CO]^+$, $[M - 3CO]^+$), 507 ($[M - {}^tBu - 2CO]^+$, $[M - 4CO]^+$), 475 ($[M - {}^tBu - 3CO]^+$), 447 ($[M - {}^tBu - 4CO]^+$), 320 ($[M - W(CO)_4]^+$, free ligand). IR/cm^{-1} (υ CO) (dichloromethane solution): 2017, m; 1898, vs, br; 1849, s. Crystals suitable for X-ray diffraction were grown by cooling a dichloromethane:hexane (1:1) solution to 0°C. Crystal data for **16**: $C_{19}H_{20}O_4S_2FeW$, M = 616.2, monoclinic, $P2_1/n$ (no. 14), a = 15.964(4) Å, b = 8.289(1) Å, c = 16.714(4) Å, β = 113.12(2)°, V = 2034.1(7) Å^3, Z = 4, D_c = 2.012 g cm^{-3}, μ(Mo Kα) = 6.59 mm^{-1}, T = 293 K, yellow blocks; 3572 independent measured reflections, F^2 refinement, $R_1 = 0.034$, $wR_2 = 0.078$, 3079 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 50°], 245 parameters. CCDC 229589.

[1-(*tert*-Butylthiolato),1′-(phenylthiolato)ferrocene]tungsten tetracarbonyl (17): To a solution of **8** (0.05 g, 0.13 mmol, 1 equiv) in dry deoxygenated THF (15 mL) was added tungsten precursor solution (30 mL, 2.3 equiv (initial concentration: 0.01 mol dm^{-3} $W(CO)_6$ in THF)). The reaction was heated at 40 °C for 24 h, after which a small amount of product was detectable by TLC. The solvent was removed in vacuo and column chromatography (7:3 hexane:dichloromethane) enabled separation of the product from unreacted ligand to give [(FcS^t-BuSPh)W(CO)$_4$] (**17**) (0.01 g, 0.01 mmol, 8% yield). Anal. Calcd for $C_{20}H_{22}S_2FeW$: C, 42.50, H, 3.27. Found: C, 42.69, H, 3.40. ^{1}H NMR (CDCl$_3$, 270 MHz, ppm) δ 7.44−7.40 (m, 2H, C_6H_5), 7.36−7.26 (m, 3H, C_6H_5), 4.78 (t, 2H, C_5H_4), 4.69 (t, 2H, C_5H_4), 4.44 (t, 2H, C_5H_4), 4.42 (t, 2H, C_5H_4), 1.38 (s, 9H, CH$_3$). Mass spectrum (*m*/*z*): 678 ([M]$^+$), 649 ([M − CO]$^+$), 617 ([M − ^{t}Bu]$^+$, [M − 2CO]$^+$), 596 ([M − ^{t}Bu − CO]$^+$, [M − 3CO]$^+$), 535 ([M − ^{t}Bu − 3CO]$^+$), 509 ([M − ^{t}Bu − 4CO]$^+$), 382 ([M − W(CO)$_4$]$^+$, free ligand). IR/cm^{-1} (υ CO) (dichloromethane solution): 2018, m; 1899, vs, br; 1853, s.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams for **1**, **5**, **9**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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