

Toward New Magnetic, Electronic, and Optical Materials: Synthesis and Characterization of New Bimetallic Tetrathiafulvalene Tetrathiolate Building Blocks

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Metal coordination complexes of tetrathiafulvalene (TTF) have long been proposed to be interesting building blocks to new electronic, optical, and magnetic materials. Presented herein are the synthesis and characterization of the first examples of early and late transition metal homobimetallic coordination complexes of tetrathiafulvalene tetrathiolate (1). We have prepared the compounds $\text{Cp}_2\text{TiS}_2\text{TTFS}_2\text{TiCp}_2$ (4), $\text{Cp}_2^*\text{TiS}_2\text{TTFS}_2\text{TiCp}_2^*$ (5), and $(\text{PPh}_3)_2\text{PtS}_2\text{TTFS}_2\text{Pt}(\text{PPh}_3)_2$ (6) and characterized these compounds by ^1H NMR, DNMR, UV-vis-NIR, elemental analysis, FAB-MS, electrochemistry, etc. The electronic spectral data of the Ti complexes indicate a strong LMCT band, which is consistent with the ability of the metal to act as an acceptor and the TTF as a donor. These compounds have been preliminarily shown to form charge-transfer complexes with TCNQ. In addition, complex 4 was also found to undergo an interesting transmetalation reaction with $\text{Ni}(\text{dppp})\text{Cl}_2$. This type of reaction affords the possible synthesis of heterobimetallic complexes of TTF. Discussion pertaining to the potential of materials based on metal-TTF hybrid molecules is also presented.

Introduction

In the development of new materials, it is recognized that building blocks of appropriate molecules must be assembled into three-dimensional structural architectures with control over molecular orientation. The solid-state orbital connectivity derived from controlled assembly determines electronic band structure, local magnetic interactions, and polarizability. These fundamental properties are at the heart of electrical conductivity, bulk magnetism, and optical nonlinearities found in numerous organic, inorganic, and polymeric materials. The development of organic solid state materials depends on the synthesis of well-defined building blocks with appropriate electronic structures, followed by controlled solid-state assembly of the blocks. While interesting building blocks continue to be synthesized, the synthesis of solids with desirable three-dimensional arrangements remains a fundamental problem in solid-state chemistry. Some success has been accomplished using directed molecular assembly to control the structure¹ and properties in optical² and magnetic materials.^{3,4}

One very interesting set of building blocks that have been used to assemble molecular electronic materials are metal bisdithiolene complexes. Early fundamental research on bisdithiolene coordination complexes (2, Figure 1) paved the way for the development of these compounds as electronic and optical materials.⁵ The work of Interrante⁶ and Miller and Epstein⁷ pioneered the way for the

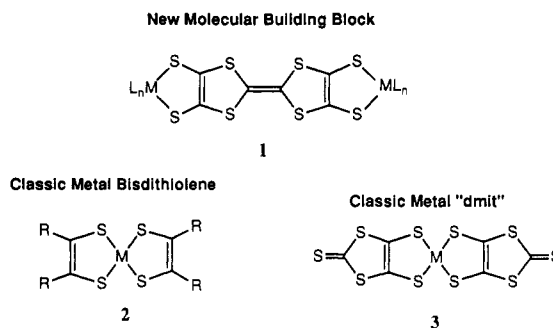


Figure 1.

continual development of metal bisdithiolenes as electronic materials. While most metal bisdithiolenes are semiconductors,⁸ certain anionic Pt salts of 2 (e.g., $\text{R} = \text{CN}$) exhibit metallic conductivity at higher temperatures. However, the metallic state in these complexes is unstable, and at lower temperatures the materials undergo a Peierls transition.⁹ Subsequently it was found that metal complexes of the related ligand 4,5-dimercapto-1,3-dithiol-2-thione (dmit, 3) can form a more stable metallic state. In fact, the one-dimensional $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ remains metallic¹⁰ to below 4 K due to a multi-Fermi surface,¹¹ and a number of $\text{M}(\text{dmit})_2$ salts have been found to be superconductors under pressure.¹²

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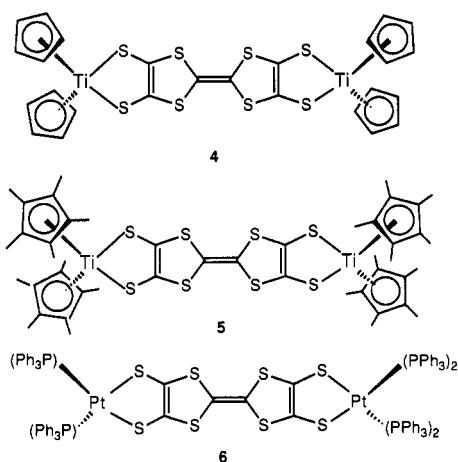


Figure 2.

A set of general concepts has emerged from the study of materials derived from metal-bisdithiolene and metal-dmit complexes. It is found that structures where the d_{z^2} molecular orbital of the metal atom can overlap to form a 1-D linear electronic chain of metal σ bonds¹³ lead to highly conductive materials. These structures are relatives of the classic one-dimensional conductor $K_2[Pt(CN)_4] \cdot Br_{0.3} \cdot 3H_2O$ (KCP). As exemplified by KCP, the resultant structure and electronic properties in the Pt metal-bisdithiolene salts⁹ are highly sensitive to both stoichiometry and the counterions. Structures containing segregated stacks of oxidized TTFs and linear chains of reduced $M(dmit)_2$ molecules can also be highly conductive. It is clear in these materials that the TTF radical cation plays an important role in the transport properties of these materials.¹⁴

We have been interested in using neutral molecules of the general structural type 1 as building blocks to new electronic, optical, and magnetic materials. We are hoping to build architectures which take advantage of the electrical properties produced by linear metal atom chains and stacks of TTF molecules,¹⁵ built from a single building block molecule. We would expect that such materials could lead to one-dimensional two-band materials similar to TTF- $[Ni(dmit)_2]_2$. In addition, we hope to examine intra- and intermolecular spin interactions in bimetallic TTF hybrid materials.

We present here the first synthesis and characterization of monomeric bimetallic tetrathiafulvalene tetrathiolate (1) building blocks. We have prepared and characterized the complexes 4–6 (Figure 2) using NMR, dynamic NMR, IR, UV-vis-NIR, cyclic voltammetry, FAB mass spectrometry, and elemental analysis. The ability of these compounds to form charge-transfer complexes was also examined. The Cp_2Ti complex (4) is especially interesting since it has been shown that related compounds can

undergo transmetalation reactions to give new metal centers.¹⁶ We have investigated these reactions, and also presented are preliminary data on the transmetalation chemistry of compound 4.

The melding of the tetrathiafulvalene (TTF) and transition-metal structures may allow directed structural control through the propensity of TTF to form stacked structures^{12,15} and/or through coordination geometries similar to coordination complexes of bisdithiolenes.⁵ Hence both the TTF unit and the metal in 1 may afford new opportunities for the use of solid-state assembly to build new architectures (7, Figure 3). In fact, unique structural motifs based on metal-TTFS₄ building blocks were first proposed by Hoffman¹⁴ and co-workers. Hoffman proposed new ribbon (8), stacked layer-forming (9), two-dimensional layer (10), and zigzag layer (not shown) structures as shown in Figure 3. One unfortunate reality is that all of the proposed structures, except 7 will be hopelessly insoluble.¹⁷

Molecular bimetallic complexes represented by 1 not only may act as new electronic materials but also may lead to novel magnetic materials. The TTFS₄ framework should allow spin interaction between the two metal centers via superexchange.^{3,18} In addition, a one-electron oxidation should drive a spin ordering of the molecule through intramolecular antiferromagnetic coupling of spins (Figure 4). Our major thrust is in the preparation of new ferrimagnetic materials based on our proposal of using mixed stack charge-transfer complexes¹⁹ of bimetallic TTFS₄ complexes (Figure 5). In this case, the one electron oxidation occurs due to charge-transfer salt formation and intermolecular antiferromagnetic coupling can occur between the donor-acceptor molecules. Structural networks based on these new building blocks have the potential to open up new opportunities in magnetic, electronic, and optical materials and the exploration of the chemistry of materials.

Results and Discussion

Synthesis and Characterization of L_nMS_2 -TTFS₂ML_n. Since the synthesis of the TTFS₄⁴⁻ has been known for some time,²⁰ it would seem the synthesis of bimetallic coordination complexes of TTFS₄⁴⁻ would be straightforward. To our knowledge, however, there have been no reports of the preparation of such compounds prior to this work. We have found that the synthesis of metal-TTFS₄ compounds is fraught with multiple and difficult obstacles. All of the isolated TTFS₄ coordination compounds, in our experience, are sensitive to oxygen and water. Complexes represented by 1 are also neutral metal complexes and not metal salts, making these compounds more reactive than 2 and 3. Although the syntheses of related polymeric or oligomeric compounds¹⁷ prepared from metal salts and TTFS₄⁴⁻ have been reported, these polymer/oligomers have not been well-characterized and must contain multiple impurities derived from the synthesis of the ligand, TTFS₄⁴⁻. In addition, complete

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(20) Schumaker, R. R.; Engler, E. M. *J. Am. Chem. Soc.* 1977, 99, 5521. While the Schumaker and Engler preparation of 13 is useful for the synthesis of tetrathioalkyl derivatives of TTF, it is generally not useful for the preparation of well-defined inorganic compounds.

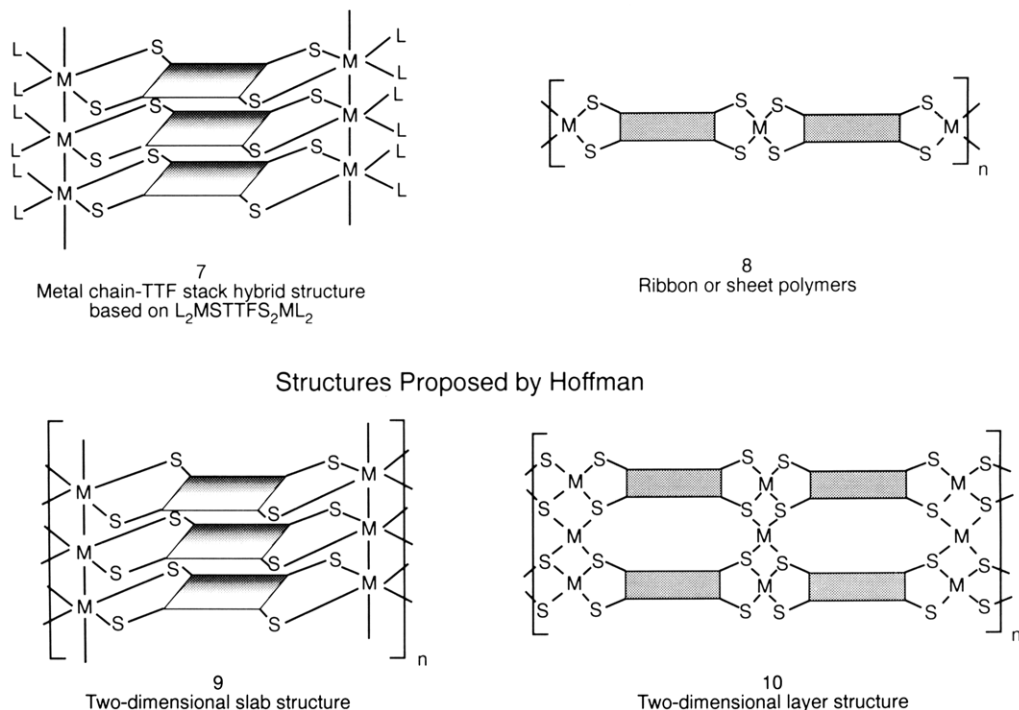


Figure 3.

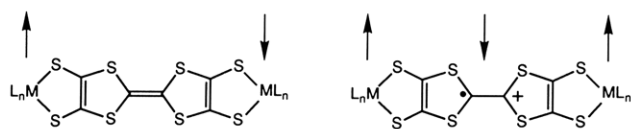
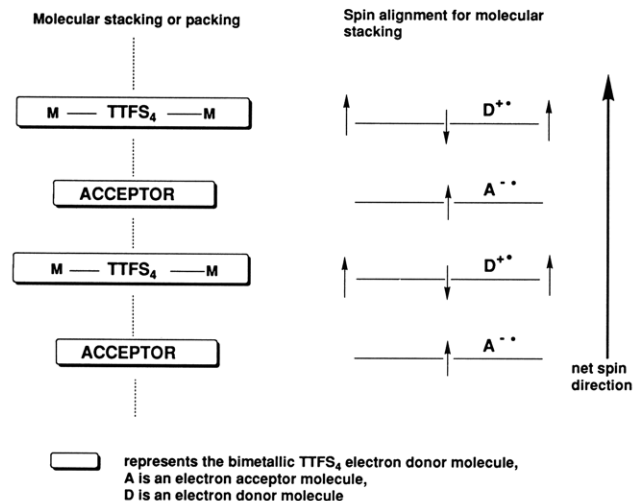
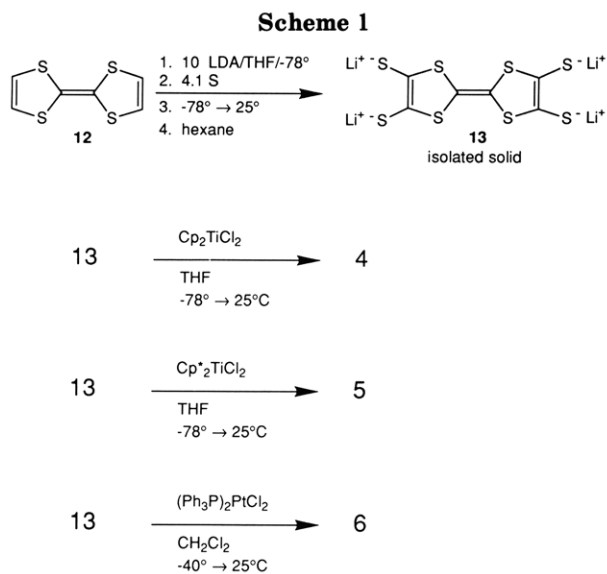
Figure 4. Spin interactions in bimetallic $TTFS_4$ complexes. Complexes shown are based on M having $S = 1/2$ ground state.

Figure 5. Proposal for new molecular ferrimagnets based on mixed-stack, charge-transfer complexes.

characterization as well as control over the solid-state properties of these compounds is impossible since they are completely insoluble. We have recently solved this problem with the synthesis of the ligand²¹ by providing a method of making pure $TTFS_4^{4-}$ (Scheme 1). We believe this has been a major problem in the development of metal- $TTFS_4$ compounds (1) as new materials.

There are two reported methods to synthesize the $TTFS_4^{4-}$ ligand (other than our recently reported method²¹). Schumaker and Engler's²⁰ preparation of 13



produces ketones or carbonates and/or anionic byproducts (which are derived from the reaction of dithiapendione and sodium methoxide or methyl lithium), which can compete for metal coordination sites with ligand 13. This must lead to a mixture of products and subsequently cause difficulties in purification.

Theoretically compound 13 could also be synthesized by the treatment of TTF with 4 equiv of LDA,^{22,23} followed by 4 equiv of sulfur. However, recent work in our lab²¹

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(26) Although, the LDA route does not generally lead to $TTFS_4^{4-}$ derivatives, the tetralithiated TTF can be effectively quenched with Se or Te metal. This method is generally used to synthesize $TTFS_4^{4-}$ and $TTFTe_4^{4-}$ derivatives, see: (a) ref 25; (b) ref 22; (c) Okada, N.; Yamochi, H.; Shinozaki, F.; Ohima, K.; Saito, G. *Chem. Lett.* 1986, 1861.

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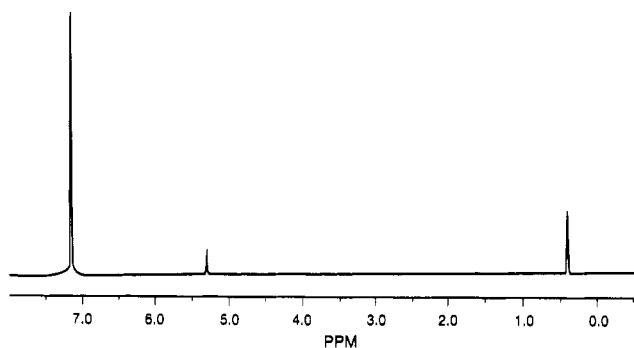


Figure 6. ^1H NMR of $\text{Cp}_2\text{TiS}_2\text{TTFS}_2\text{TiCp}_2$ (4). The peak at 5.3 ppm is the compound, and the remaining peaks are residual protons from solvent (C_6H_6 and H_2O).

and work by Zambounis and Mayer²⁴ and Chiang^{25,26} demonstrates that this route is generally ineffective in the synthesis of TTFS_4^{4-} . In addition, we²¹ and Zambounis²⁴ have independently found that treatment of TTF with 4 equiv²² of LDA does not cleanly give "TTFLi₄". In fact, the desired ligand is produced only as a minor product with the major products being the mono-, di-, and trilitiated species. Fortunately, we were able to circumvent²¹ this problem by using excess LDA and a hexane precipitation of the desired product 13 in 85% yield. We have found that filtration of the reaction mixture after the uptake of sulfur, followed by precipitation of 13 with hexanes (drybox), and subsequent washing of 13 with hexane removes diisopropylamine (DIA), hexane-soluble impurities, and THF-insoluble impurities. The removal of the coordinating ligand DIA and higher polysulfides greatly improves the purity of the isolated crude product and hence makes the synthesis of pure metal- TTFS_4^{4-} compounds easier.

We have found compound 13 is golden in color and extremely air and water sensitive. The compound can be handled safely in a glovebox. As a consequence of this instability, we have found it impossible to purify *any* resulting metal complexes if the slightest green discoloration of 13 does occur due to decomposition (probably oxidation). However, by using our method to synthesize pure TTFS_4^{4-} (13), the ligand is available for the formation of a variety of metal-TTF hybrid materials. In Scheme 1 is shown the synthesis of three new compounds based on this method.

The bimetallic TTF complex, 4, is synthesized by addition of TTFS_4^{4-} (13) in THF to two equivalents of Cp_2TiCl_2 in THF at -78°C (Scheme 1). The product 4 can be isolated by precipitation in ca. 30% yields and is air and water sensitive. Due to the oxophilic nature of titanium(IV), compound 4 decomposes rapidly on silica or alumina. The compound also decomposes in chlorinated solvents presumably through scission of the Ti-S bond.¹⁶ We have observed this decomposition reaction via NMR in C_6D_6 upon the addition of CH_2Cl_2 and via UV-vis studies.

Compound 4 exhibits a singlet (5.3 ppm) in the ^1H NMR (C_6D_6 , Figure 6). In coordinating solvents such as THF- d_5 or CD_3CN the Cp ring degeneracy is removed giving rise to two broad absorptions. Upon evaporation of either of these NMR solvents and redissolving the compound in C_6D_6 one sees a single peak at 5.3 ppm. Compound 4 was also characterized by the observation of the known dynamic behavior in Cp_2Ti dithiolene coordination complexes.¹⁶ In $\text{C}_6\text{D}_6\text{CD}_3$ we have observed a complex set of

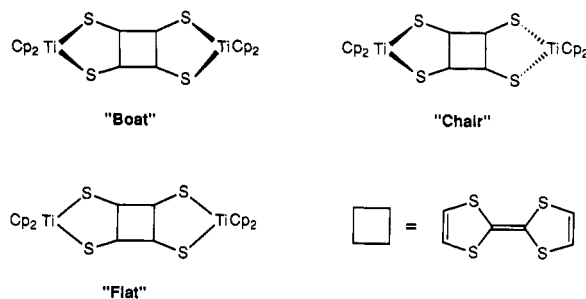


Figure 7.

dynamic conformational behavior representing the ring flipping ("boat"–"chair" equilibrium) of "dithiolene" ends of the TTF spacer and the conformational twisting of a π -bonded "flat" structure (Figure 7).¹⁶ It is known that Cp_2Ti dithiolene complexes in general do not adopt a completely flat structure, since the π orbital overlap is greatest from the S lone pairs to the Ti center when these structures are bent.¹⁶ We find two resonances at 5.41 and 5.35 ppm at 60°C (Figure 8). We postulate that these two resonances represent two distinct conformer populations—the broad peak at 5.35 ppm represents the dynamic equilibrium between the less stable "boat" and "chair" forms. Upon cooling the solution to 30°C , we observe the freezing out of "boat" and "chair" forms. We are postulating that the four resonances represent the Cp rings over the TTF ring and away from the TTF ring in both the "chair" and "boat" conformations. At $\approx 20^\circ\text{C}$ we observe that the peak at 5.41 ppm starts decoalesces into two resonances, representing the freezing out of the twist conformers of the "flat" structure. At -53°C , we observe the freezing out of some of the Cp ring movement. Enhanced steric requirements of these compounds cause the temperatures for the freezing out the Cp rings to be higher relative to simple monometallic dithiolene complexes.²⁷

The UV-vis-NIR of 4 (C_6D_6) follows Beer's law up to concentrations of 2×10^{-4} M precluding any aggregation in our NMR experiments. In THF the complex exhibits higher energy absorbances attributable to Cp and TTF at λ (ϵ) = 225 (53 800), 319 (22 300), 454 (4100), and 760 (7500). In C_6H_6 considering the TTF peak and the NIR band, equal intensity absorbances are observed at 470 and 780 nm (Figure 9). The long wavelength 760 nm (ϵ = 7500) is preliminarily assigned to a LMCT band (TTF \rightarrow Ti(IV)).²⁸ Compound 4 is optimally set up for LMCT given the electron-donating nature of TTF and the electron-accepting ability of Ti(IV). We have yet to examine the excited state of this complex; however, we expect it to be long lived. Such compounds are reminiscent of the strong reductants in photosynthesis, especially if we are generating the powerful reductant, Ti(III). Such LMCT bands in d^0 metal complexes are rare and are only recently being explored for their potential as photochemical reductants and luminescent materials.^{29,30}

The electrochemical characterization (Figure 10) of 4 (0.2 M TBAPF₆ in CH_3CN vs Ag wire) shows two reversible

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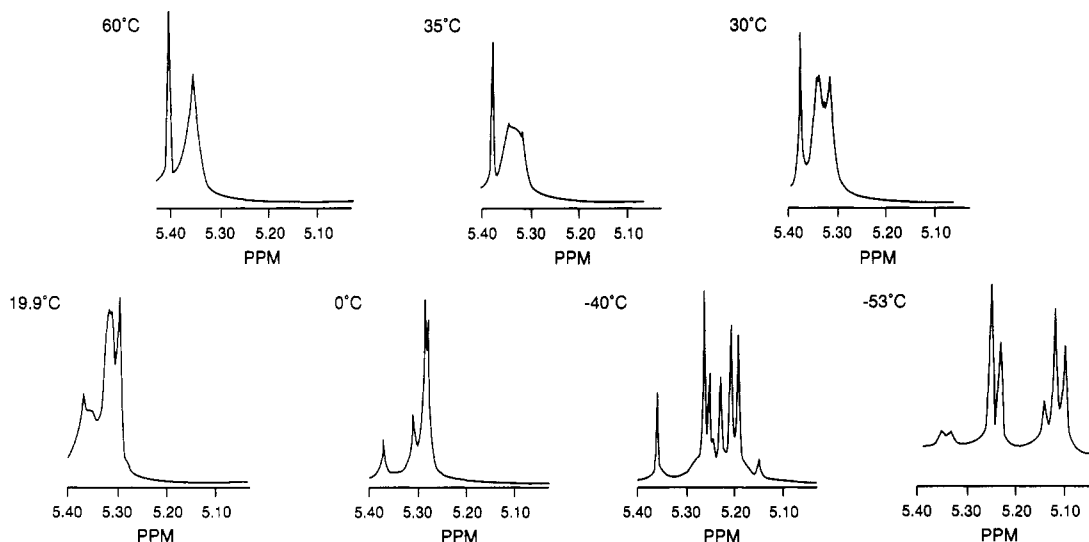


Figure 8. Dynamic NMR behavior of $\text{Cp}_2\text{TiS}_2\text{TTFS}_2\text{TiCp}_2$ (4).

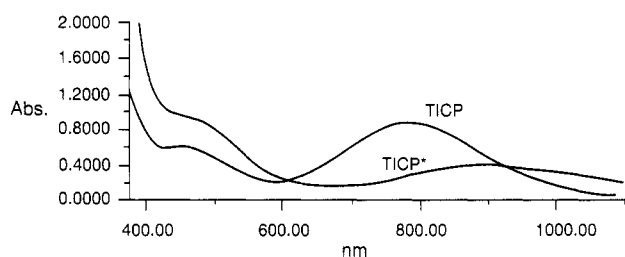


Figure 9. UV-vis-NIR of $\text{Cp}_2\text{TiS}_2\text{TTFS}_2\text{TiCp}_2$ (4) and $\text{Cp}^*_2\text{-TiS}_2\text{TTFS}_2\text{TiCp}^*_2$ (5).

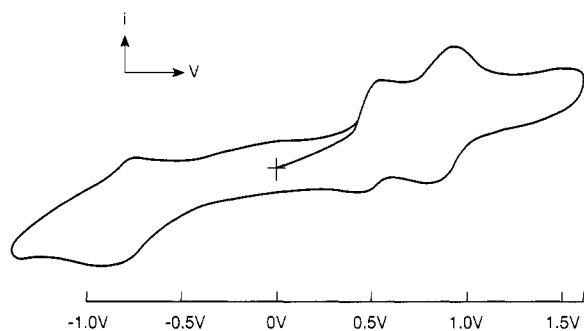
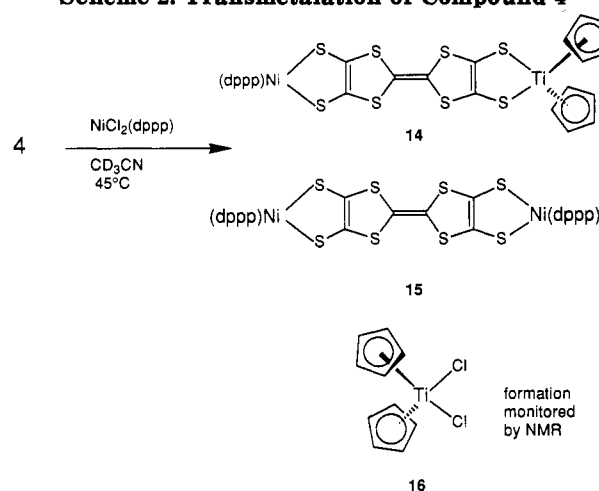


Figure 10. Cyclic voltammetry of compound 4.

oxidations at $E_{1/2} = 0.5$ V (TTF/TTF⁺) and $E_{1/2} = 0.85$ V (TTF⁺/TTF²⁺). As a comparison, the cyclic voltammetry of (tetrathiomethyl)tetrathiafulvalene (TTF(SMe)₄) under the same conditions shows two reversible oxidations at $E_{1/2} = 0.64$ V (TTF(SMe)₄/TTF(SMe)₄⁺) and $E_{1/2} = 0.88$ V (TTF(SMe)₄⁺/TTF(SMe)₄²⁺). In addition, we observe the Ti(IV)/Ti(III) couple at -0.85 V which is consistent with the electrochemistry observed for titanium dithiolene complexes.¹⁶ The electrochemistry also supports a molecule well designed for a long-lived LMCT excited state since the Ti(IV) center can fairly easily accept an electron from the TTF. The TTF moiety is, of course, a stable aromatic radical cation and helps to stabilize the excited state, possibly leading to enhanced luminescence.

The bimetallic complex $\text{Cp}_2^*\text{TiS}_2\text{TTFS}_2\text{TiCp}_2^*$ (5) is synthesized in the exact same manner as the bimetallic $\text{Cp}_2\text{TiS}_2\text{TTFS}_2\text{TiCp}_2$ (4). The ligand TTFS_4^{4-} (13) is added to $\text{Cp}_2^*\text{TiCl}_2$ in a similar fashion. After solvent removal, the solid product is isolated by Soxhlet extraction with hexanes. The product, 5, is also quite air and water sensitive and decomposes on silica.

Scheme 2. Transmetalation of Compound 4



The physical properties of the Cp^* complex 5 mirror those of the Cp complex 4. The ^1H NMR (C_6D_6) shows a singlet and a doublet centered at 1.7 ppm. When this is warmed up to $\approx 60^\circ\text{C}$, these two sets of peaks approach coalescence, representing the solution conformer populations. The vis-NIR spectra (Figure 9, C_6D_6) of 5 shows a very similar absorbance to compound 4 at 470 nm. There is, however, a red shift of the NIR absorbance for the Cp^* complex, 5. The NIR band for 5 centered at 920 nm is shifted to lower energy and broadened due in part to the electron-donating effect of the Cp^* as well as steric reasons. The methyl groups on the Cp ring cause³¹ the metal LUMO³² a_1 to drop in energy as the Cp^* rings become more parallel to each other (due to steric reasons). This effectively lowers the energy of the LMCT by lowering the acceptor orbital energy.

There also appears to be a slight donating effect of the Cp_2^*Ti to the TTF as evidenced in the electrochemistry of the complex 5. The donating ability of the Cp^* ring is apparent in a negative shift of the reduction potential of the Ti(III)/Ti(IV) from -0.85 V for 4 to -1.15 V for 5. The TTF couples are, as expected, shifted to 0.35 and 0.70 V.

Transmetalation of $\text{Cp}_2\text{TiS}_2\text{TTFS}_2\text{TiCp}_2$ (4). Work by Rauchfuss¹⁶ and co-workers has shown that Ti disele-

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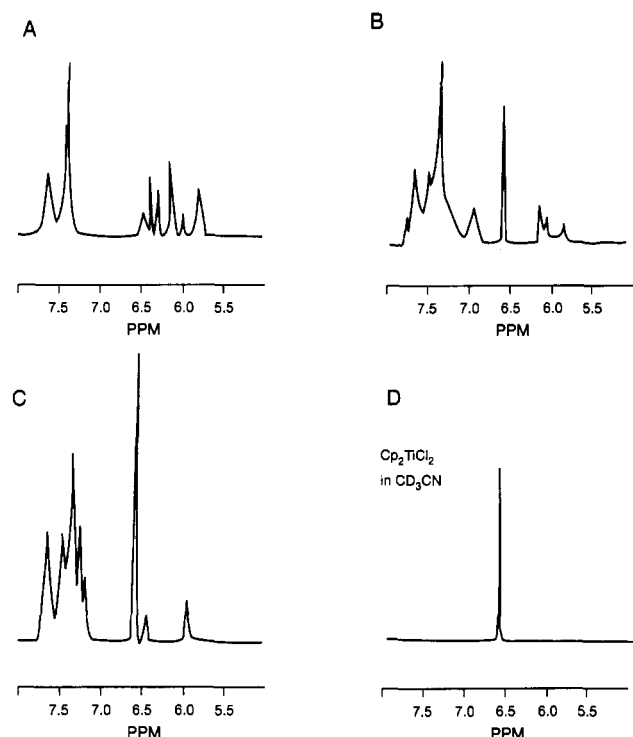


Figure 11. (A) Reaction mixture (Scheme 2) at 25 °C. (B) Reaction mixture at 45 °C. (C) Reaction mixture at 45 °C after 0.5 h. (D) Cp_2TiCl_2 standard.

nene complexes (compound 2, where S is replaced by Se, $\text{R} = \text{CO}_2\text{CH}_3$) can undergo very interesting transmetalation reactions with $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2$ ($\text{Ni}(\text{dppp})\text{-Cl}_2$). The product was found to be $\text{Ni}(\text{Se}_2\text{C}_2(\text{CO}_2\text{-CH}_3)_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)$. The exploitation of the halophilicity of titanium(IV) and the thiophilicity of the later transition metals makes these transmetalation reactions possible. This chemistry offers us some very interesting possibilities such as the stepwise development of heterobimetallic TTFs_4 complexes. We therefore examined the transmetalation reaction of $\text{Cp}_2\text{TiS}_2\text{TTFs}_2\text{-TiCp}_2$ (4) with $\text{Ni}(\text{dppp})\text{Cl}_2$ by NMR (Scheme 2).

Upon treatment of compound 4 with $\text{Ni}(\text{dppp})\text{Cl}_2$ in dry CH_3CN at room temperature, we observe no reaction. However, upon slowly increasing the temperature of the NMR sample chamber, we observe the growth of a singlet at 6.6 ppm at 45 °C, indicative of Cp_2TiCl_2 (16) formation (Figure 11B,C). In the same CD_3CN solvent, a spectrum of pure Cp_2TiCl_2 appears as a singlet (Figure 11D) at the exact chemical shift of the Cp_2TiCl_2 observed in the NMR tube experiment. The reaction is near completion after 0.5 h. The transmetalation of Ti in a thiolene complex as observed here is rare. Given that our compounds decompose in halogenated solvents, we are also currently investigating the reaction of compounds such as 4 and 5 with conventional organic halides. These preliminary results are quite interesting as representative building block reactions to linear, 1-D chains.

Charge-Transfer Complexes. We have investigated the ability of the $\text{Cp}_2\text{TiS}_2\text{TTFs}_2\text{TiCp}_2$ (4) to form charge-transfer complexes with tetracyanoquinodimethane (TCNQ) and chloranil. Our interest is in the controlled formation of both segregated stacks for conductive materials and mixed stack complexes for magnetic materials.¹⁹ A THF solution of 4 and an CH_3CN solution of TCNQ were mixed and pentane was allowed to diffuse into this dark solution. After 7 days, the resulting blue-black

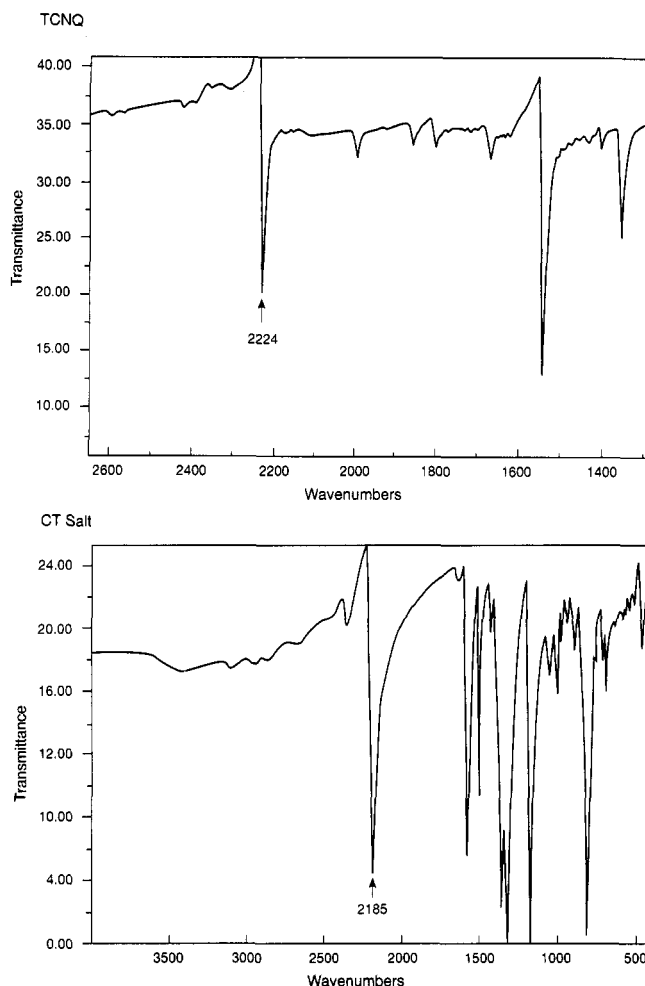


Figure 12. Infrared spectra of (top) TCNQ (KBr) and the (bottom) charge-transfer complex made from compound 4 and TCNQ. The CN stretching frequency is noted by the arrows.

compound was analyzed by IR. We find a bathochromic shift of 39 cm^{-1} (from 2224 to 2185 cm^{-1} , Figure 12) in the CN stretching frequency of the TCNQ which represents a charge transfer of one electron per TTF-TCNQ unit. The molecule TCNQ alone has a CN stretching frequency of 2224 cm^{-1} . It has been shown by Cowan and co-workers that a shift in the CN stretching frequency can be correlated to the degree of charge transfer in charge-transfer complexes.³³ Chloranil, a weaker electron acceptor, fails to react with 4. Further investigation and growth of charge transfer complexes is ongoing.

Synthesis of Other $\text{L}_n\text{MS}_2\text{TTFs}_2\text{ML}_n$ Compounds. We have reacted 13 in THF with *cis*-bis(triphenylphosphine)platinum(II) chloride (*cis*- $(\text{Ph}_3\text{P})_2\text{PtCl}_2$) in CH_2Cl_2 ($-40 \rightarrow 25$ °C, 18 h) to yield platinum complex 6. The crude product was isolated by precipitation with hexane and purified by passing the compound through Sephadex-LH-20 (twice, 5:1 $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}$). Solvent removal afforded an orange-brown solid. The compound was soluble in CH_2Cl_2 and highly air sensitive requiring that all manipulations be performed in a drybox.³⁴ The IR spectra shows the presence of phosphine ligands. The UV-vis (THF) spectra shows peaks at 280 (λ_{max}), 250, 340, and 450 nm (TTF, v br) and a very weak intensity peak

(33) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* 1981, 103, 2442.

(34) Caution should be taken since on one occasion an insoluble solid isolated from this reaction was found to be pyrophoric in air.

at 720 nm (d-d transition). Peaks for pure TTF (THF) occur at 310 (λ_{\max}), 290, 380, and 450 nm. The UV-vis of the ligand 13 shows peaks at 240 nm (λ_{\max}) and 330 nm. The ^1H NMR (CDCl_3) of 6 shows three peaks: 7.50 (triplet of doublets, $J = 9$ Hz, $J = 2$ Hz), 7.12 (t, $J = 8.6$ Hz), 7.18 ppm (triplet of doublets, $J = 8.6$ Hz, $J = 2.5$ Hz). The coupling patterns indicate ^{31}P - ^1H coupling. Other than residual protons from solvent, these are the only observed absorptions. A ^{13}C NMR (75 MHz, CDCl_3) shows the TTF absorptions, in addition to the phenyl carbons. The ^{31}P NMR (external reference, $(\text{MeO})_3\text{P}$, (CDCl_3)) shows only two absorptions, a singlet (13.85 ppm) due to ^{31}P attached to spin inactive Pt isotopes and a doublet (29.4 and -1.3 ppm) due to ^{31}P coupled to ^{195}Pt ($J = 3730$ Hz). FAB mass spectra show the molecular ion at m/z 1768, and the isotopic cluster matched a computer-generated theoretical M^+ peak.

We have also attempted to synthesize the $\text{Cp}_2\text{VS}_2\text{TTFs}_2\text{-VCp}_2$ complex. Since V should have a $S = 1/2$ ground state, such complexes should exhibit the type of spin interactions shown in Figure 4. However, attempts to date have failed to produce a compound of sufficient purity to be reported here. We have not observed an ^1H NMR signal³⁵ in C_6D_6 and have observed a UV-vis spectra and obtained electrochemical data all of which are consistent with the structure. It is important to point out that both the isolated product (soluble in C_6H_6) and C_6H_6 insoluble fractions are pyrophoric in air. We have experienced cases of minor fires and explosions with these compounds—we advise caution in handling these compounds.

Experimental Section

All reactions were performed under prepurified nitrogen or argon, using dry glassware. Glassware was dried in an oven overnight and then cooled under a stream of argon or nitrogen. Tetrahydrofuran and benzene were dried over Na benzophenone ketyl radical and freshly distilled prior to use. Diisopropylamine, hexane, and acetonitrile were dried and distilled from CaH_2 and stored in the glovebox. Sulfur (99.999%) was purchased from the Aldrich Chemical Company, dried under vacuum, and stored in a drybox. Tetrathiafulvalene (TTF) was purchased from Aldrich and used as received. Tetracyanoquinodimethane (TCNQ) was purchased from Aldrich and recrystallized (twice) from CH_3CN prior to use.

^1H NMR spectra were recorded at 300 MHz. Elemental analysis was performed by Midwest Microlabs, Indianapolis, IN.

Preparation of Tetrathiafulvalene Tetrathiolate (13). The reagent $n\text{-BuLi}$ (6.2 mL of a 1.6 M solution in hexane, 9.92 mmol) was added to a solution of diisopropylamine (1.4 mL, 1.01 g, 10 mmol) in dry THF (20 mL) at -78°C under argon. After stirring the solution for 0.75 h, tetrathiafulvalene (TTF, 0.20 g, 0.98 mmol) in dry THF (12 mL) was slowly added over 15 min to the LDA and the solution was stirred at -78°C for 2.5 h. During the formation of the tetralithiated TTF, the solution became bright yellow and some solid particles appeared. Elemental sulfur (0.14 g, 4.1 equiv) was suspended in 5 mL of THF and added to the reaction flask. The solution was stirred at -78°C for 1 h, then the cold bath was removed, and the solution was stirred for an additional 4 h. The brown solution was warmed to 25°C during this period. The reaction vessel was transferred into a drybox. The solution was filtered to remove any solids (including residual sulfur). Compound 13 was then precipitated by the addition of dry hexane (250 mL) to the filtrate. The complete precipitation of 13 was facilitated by cooling the solution to -20°C for a total of 0.5 h. The solution was filtered through a fritted glass funnel (medium porosity), and the solid was washed with 50 mL of hexane to remove diisopropylamine and other

soluble impurities. The solid remaining on the filter was quantitatively transferred to a clean round bottomed flask, and dry THF (≈ 90 mL) was added. The flask was sealed and removed from the drybox and then cooled to -78°C and stirred under argon for 0.5–1 h, in order to redissolve 13.

Synthesis of $\text{Cp}_2\text{TiS}_2\text{TTFs}_2\text{TiCp}_2$ (4). A solution of lithium tetrathiafulvalene tetrathiolate (13) in dry THF (90 mL, 9.8×10^{-3} M) from above (from 0.98 mmol of TTF) was cannula transferred to a stirring solution of Cp_2TiCl_2 (0.49 g, 1.96 mmol, 2 equiv) in THF (150 mL) at -78°C . The reaction was then stirred at -78°C for 1.25 h. The cold bath was then removed and the solution was stirred for 15 h, whereupon the reaction mixture slowly warmed to 25°C . The flask containing the greenish-black mixture was sealed and transferred to a glovebox, and the volatiles were removed in vacuo. Most of the solids were dissolved in boiling, dry benzene (3×30 mL) and then filtered through a fritted funnel (150 mL, M porosity) to afford a green filtrate. **CAUTION:** The solids remaining on the filter are pyrophoric in air. The product was then precipitated by the addition of dry hexanes (350 mL) to the green benzene solution. The solid product was collected by filtration and washed on the filter (15 mL, M porosity) with dry hexane to yield 0.20 g of a green solid (30% yield). ^1H NMR (C_6D_6) 5.32(s) ppm; UV-vis-NIR (THF), λ (in nm) (ϵ), 225 (53 800), 319 (22 300), 454 (4100), 760 (7500); UV-vis (C_6D_6) 470 nm, 788 nm; IR (KBr, cm^{-1}) 3130–3090 (C–H), 1438 (C=C, Cp), 1365 (C=C, TTF), 818 (C–S); electrochemistry (volts vs Ag wire, 0.2 M $n\text{-Bu}_4\text{NPF}_6$, CH_3CN) ($E_{1/2}$) 0.50 V (TTF/TTF $^+$), 0.85 V (TTF $^+$ /TTF $^{2+}$), -0.85 V (Ti $^{4+}$ /Ti $^{3+}$). Anal. Found (calcd): C, 45.54 (45.61); H, 3.10 (2.92); S, 37.15 (37.42).

Synthesis of $\text{Cp}^*\text{TiS}_2\text{TTFs}_2\text{TiCp}^*$ (5). To a solution of lithium tetrathiafulvalene tetrathiolate (13) in dry THF (100 mL, 9.8×10^{-3} M) from above (from 0.26 g of TTF, 1.27 mmol) was cannula transferred to a stirring solution of Cp^*TiCl_2 (1.0 g, 2.57 mmol, 2 equiv, 2.56×10^{-3} M) in THF (150 mL) at -78°C . The reaction was then stirred at -78°C for 1.25 h. The cold bath was then removed and the solution was stirred for 12 h, whereupon the reaction mixture slowly warmed to 25°C . The flask containing the red-black mixture was sealed and transferred to a drybox, and the volatiles were removed in vacuo. The dry solids were collected in a Soxhlet thimble and extracted with hexanes (350 mL) until the washings were colorless. **CAUTION:** The solids remaining in the thimble are pyrophoric in air. The solvent is removed to yield 240 mg of a red solid (20% yield). ^1H NMR (C_6D_6) 1.7 (singlet and doublet) ppm; UV-vis-NIR (C_6D_6), λ (in nm), 225, 319, 470, 920; for 5; electrochemistry (volts vs Ag wire, 0.2 M $n\text{-Bu}_4\text{NPF}_6$, CH_3CN) ($E_{1/2}$) 0.35 V (TTF/TTF $^+$), 0.70 V (TTF $^+$ /TTF $^{2+}$), -1.15 V (Ti $^{4+}$ /Ti $^{3+}$).

Transmetalation of 4 with $\text{Ni}(\text{dppp})\text{Cl}_2$. To a solution of $\text{Cp}_2\text{TiTTFS}_4\text{TiCp}_2$ (4, 5 mg, 7.3 μmol) in C_6D_6 was added $\text{Ni}(\text{dppp})\text{Cl}_2$ (8.0 mg, 14.6 μmol) in dry CH_3CN . The solution was cannula transferred to an NMR tube. The solution was slowly heated until a signal indicative of Cp_2TiCl_2 was seen. That temperature was 45°C . The reaction was followed by NMR (see Figure 11).

Charge-Transfer Complex Formation of 4 with TCNQ. This reaction was performed in the glovebox. A solution of $\text{Cp}_2\text{TiTTFS}_4\text{TiCp}_2$ (4, 33 mg, 48 μmol) in 35 mL of dry THF (1.4×10^{-3} M) was prepared. To this solution was added TCNQ (recrystallized twice, 13.0 mg, 64 μmol) in 6 mL of dry THF. The wide-mouth jar containing this solution mixture was placed in a larger jar which contained dry pentane. This sealed vessel was placed in the glovebox freezer at -10°C for 24 h. The solution was warmed to -5°C and left for 7 days. The blue-black powder was isolated by filtration and analyzed by IR. IR (cm^{-1}) TCNQ: 2224 (–CN); charge-transfer complex with 4 2185 (–CN, see Figure 12).

Synthesis of $(\text{Ph}_3\text{P})_2\text{PtS}_2\text{TTFs}_2\text{Pt}(\text{PPh}_3)_2$ (6). The ligand tetrathiafulvalene tetrathiolate (13) was synthesized using the procedure given above using 0.20 g of TTF (0.98 mmol). The solid remaining on the filter was quantitatively transferred to a clean round-bottomed flask, and dry THF (≈ 90 mL) was added. The flask was sealed and removed from the glovebox and then transferred (via cannula) to a flask containing 2 equiv of *cis*-bis(triphenylphosphine)platinum(II) chloride ($\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$, 1.55

(35) Kopf, H.; Wirl, A.; Kahl, W. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 137.

g, 1.98 mmol) in dry THF (90 mL) stirring at $-40\text{ }^{\circ}\text{C}$ (or $-78\text{ }^{\circ}\text{C}$) under argon. The reaction was allowed to proceed for 0.75 h and then allowed to slowly warm to room temperature over 12 h. The reaction flask is then transferred to a glovebox and the volatiles removed in vacuo. The remaining solids were taken up in CH_2Cl_2 and purified on Sephadex-LH-20 using 5:1 CH_2Cl_2 : CH_3CN as an eluent system. We have also purified the compound by dissolving the solids with CH_2Cl_2 and eluting the compounds with acetone on silica gel. Solvent removal afforded an orange-brown solid. **CAUTION:** Insoluble solids isolated as byproducts are pyrophoric in air. The IR spectra shows the presence of phosphine ligands. ^1H NMR (300 MHz, CDCl_3) 7.50 (triplet of doublets, $J = 9\text{ Hz}$, $J = 2\text{ Hz}$), 7.12 (t, $J = 8.6\text{ Hz}$), 7.18 ppm (triplet of doublets, $J = 8.6\text{ Hz}$, $J = 2.5\text{ Hz}$, patterns indicate ^{31}P - ^1H coupling); ^{31}P NMR (121 MHz, external reference, $(\text{MeO})_3\text{P}$, CDCl_3) 13.85 ppm (s, ^{31}P attached to spin-inactive Pt isotopes), 29.4 and -1.3 ppm ("doublet", ^{31}P coupled to ^{195}Pt ($J = 3730\text{ Hz}$)); UV-vis (THF) 280, 250, 340, 450 nm (TTF, v br), and a very weak intensity peak at 720 nm (d-d transition); IR (KBr, cm^{-1}) major absorptions, 1483 (s), 1433 (s), 1183 (m), 1150 (s), 1100 (vs), 1000 (m), 750 (vs), and 700 (vs) (TTF major IR peaks at 795, 780, 730, 673 cm^{-1}). FAB-MS m/z (all peaks are isotopic cluster peaks mainly due to five isotopes of Pt (e.g., ^{194}Pt

(33%), ^{195}Pt (34%), ^{196}Pt (25%), assignment, relative intensity) 1768 (M^+ , 1), 1710 ($\text{M} - \text{C}_2\text{H}_2\text{S}$, 2), 1680 ($\text{M} - \text{C}_2\text{S}_2$, 3), 854 ($\text{C}_3\text{S}_3\text{-Pt}(\text{PPh}_3)_2^+$, 50), 720 ($(\text{Pt}(\text{PPh}_3)_2^+$, 50); the isotopic cluster peak at $m/z = 1768$ matched a computer-generated theoretical M^+ peak. Elemental analysis on a sample purified on Sephadex was found to be (calculated for $\text{C}_{78}\text{H}_{60}\text{S}_8\text{P}_4\text{Pt}_2 \cdot 1\text{CH}_2\text{Cl}_2$) C, 51.24 (51.21); H, 3.46 (3.37); S, 13.06 (13.84). Elemental analysis on a sample purified on alumina II was found to be (calculated for $\text{C}_{78}\text{H}_{60}\text{S}_8\text{P}_4\text{Pt}_2 \cdot 1\text{CH}_2\text{Cl}_2$) C, 51.39 (51.21); H, 3.50 (3.37).

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Supplementary Material Available: IR spectrum of compound 4 (1 page). Ordering information is given on any current masthead page.