

Novel Bonding Modes between Tetrathiafulvalenes (TTFs) and Transition Metal Centers: π -Bonding and Covalent TTFSiMe₂–ML_n Coordination to Platinum

Mathuresh N. Jayaswal,^[a] Harmel N. Peindy,^[a] Fabrice Guyon,^{*,[a]} Michael Knorr,^{*,[a]} Narcis Avarvari,^[b] and Marc Fourmigué^[b]

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Two novel strategies for coordinating TTF to transition metal centers have been developed. The reaction of tetrathiafulvalene (TTF) or 3,4-dimethyltetrathiafulvalene (*o*-Me₂TTF) with [Pt(η^2 -C₂H₄)(PPh₃)₂] leads to the π complexes [Pt(η^2 -TTF)(PPh₃)₂] (**1**) and [Pt(η^2 -*o*-Me₂TTF)(PPh₃)₂] (**2**), respectively. An X-ray crystallographic study performed on **2** confirmed, that TTFs act as a π acidic ligand. NMR studies revealed the existence, in solution, of an equilibrium between free and complexed TTF. Dilithiation of *o*-Me₂TTF and subsequent silylation with ClSiMe₂H afforded 3,4-dimethyl-

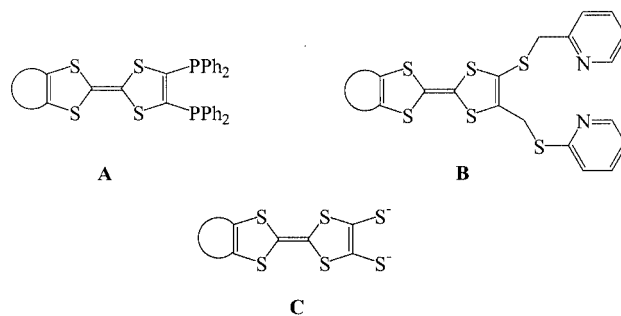
3',4'-(dimethylsilyl)tetrathiafulvalene (**3**), which has been structurally characterized. **3** reacts by oxidative addition across [Pt(η^2 -C₂H₄)(PPh₃)₂] to give [Pt(η^2 -*o*-(SiMe₂)₂-TTFMe₂)(PPh₃)₂] (**4**), in which the TTF ligand is covalently ligated to platinum via SiMe₂ bridges. The redox properties of **3** and **4** have been investigated by cyclic voltammetry. Strong cathodic shifts of the two redox processes were observed for **4**, implying the TTF core.

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Introduction

From the research devoted to novel functionalized tetrathiafulvalenes (TTFs) has emerged, in the past few years, the synthesis of derivatives incorporating substituents allowing the coordination to transition metal fragments.^[1] Such molecules are particularly interesting in molecular materials science for the elaboration of hybrid organic/inorganic multifunctional materials.^[2] Two main strategies have been used for the synthesis of transition metal complexes incorporating the TTF unit: (i) the functionalization of TTFs with phosphane (**A**) or pyridine ligands (**B**) taking advantage of the donor coordinating properties of these substituents,^[3] and (ii) the coordination of metal fragments to the tetrathiolate or dithiolate tetrathiafulvalene (TTFs₄⁴⁻ and TTFs₂²⁻ (**C**), respectively) via covalent metal-ligand bonds (Scheme 1).^[4]

Organometallic chemistry, however, offers additional alternative routes to link a metal center to an organic substrate, such as oxidative addition and π -coordination. Starting with a Pt⁰(PPh₃)₂ fragment, we present herein two novel



Scheme 1. Schematic drawings of TTF derivatives used as ligands

synthetic approaches for the development of organometallic complexes incorporating the TTF unit. Firstly, since there are no reports of studies devoted to the synthesis of transition metal complexes incorporating a π -ligated TTF unit, it was tempting to evaluate the ability of TTF to act as a π -acidic ligand. Our second strategy is based on the functionalization of TTFs with SiR₂–H moieties followed by the oxidative addition of the Si–H bond to the low valent platinum center. In this paper we describe the synthesis and characterization of the complexes [Pt(η^2 -TTF)(PPh₃)₂], [Pt(η^2 -*o*-Me₂TTF)(PPh₃)₂], and [Pt{*o*-(SiMe₂)₂TTFMe₂}(PPh₃)₂], which, to the best of our knowledge, represent the first examples of two novel bonding modes between TTF derivatives and transition metal centers i.e. π bonding and covalent bonding via an SiR₂ bridge.

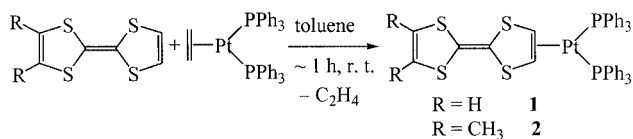
^[a] Laboratoire de Chimie des Matériaux et Interfaces, Université de Franche-Comté, Faculté des Sciences et des Techniques, 16, Route de Gray, 25030 Besançon Cedex, France
E-mail: michael.knorr@univ-fcomte.fr

^[b] Laboratoire de Chimie Inorganique, Matériaux et Interfaces, Université d'Angers, FRE 2447 CNRS, 2 Boulevard Lavoisier, 49045 Angers, France

Results and Discussion

Synthesis and Characterization of $[\text{Pt}(\eta^2\text{-TTF})(\text{PPh}_3)_2]$ (**1**) and $[\text{Pt}(\eta^2\text{-}o\text{-Me}_2\text{TTF})(\text{PPh}_3)_2]$ (**2**)

The displacement of the ethylene ligand in $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ by other olefins such as styrene, propenoates, cycloalkenes, tetracyanoethylene, allenes, and other olefinic compounds represents a convenient method of preparing Pt^0 complexes of the type $[\text{Pt}(\text{olefin})\text{PPh}_3)_2]$, since volatile ethylene can be easily removed. The olefinic structure of TTF led us to investigate its reactivity towards the reactive starting material $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$. After stirring a solution of $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ in toluene with a slight excess of TTF for 1 hour, concentration and addition of heptane afforded bright yellow $[\text{Pt}(\eta^2\text{-TTF})(\text{PPh}_3)_2]$ (**1**) (Scheme 2). The coordination of TTF via the $\text{H}-\text{C}=\text{C}-\text{H}$ bond can be inferred unambiguously from the NMR spectra. Thus, in the proton NMR spectrum, two olefinic hydrogen atoms give rise to a broadened triplet at $\delta = 3.96$ with a $^3J_{\text{P,H}}$ coupling of 2.5 Hz, and an additional $^3J_{\text{Pt,H}}$ coupling of 60.2 Hz. For comparison, the ethylene protons of $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ resonate at a much higher field ($\delta = 2.14$ ppm). Furthermore, two singlets can be seen at $\delta = 6.35$ and 6.32 ppm in an approximate ratio of 1:1. These resonances can be interpreted by the existence, in solution, of an equilibrium between free and complexed TTF. This is corroborated by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum which displays two singlets at δ 27.8 and 16.1 in an approximate ratio of 3:1, flanked by platinum satellites ($^1J_{\text{P,Pt}} = 3444$ and 4083 Hz, respectively). The more intense system centered at 27.8 ppm can be attributed to the $(\text{PPh}_3)_2\text{Pt}$ fragment complexed by the TTF. Note that the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the starting material $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ consists of a singlet at δ 35.8 with a $^1J_{\text{P,Pt}}$ coupling of 3741 Hz. The second system centered at $\delta = 16.1$ ppm can be tentatively assigned to the platinum fragment $[\text{Pt}(\text{PPh}_3)_2]$, resulting from the decomplexation of TTF, which may be stabilized by weak interactions with the sulfur atoms. The reversible coordination/decoordination of an olefin has already been reported in the case of the complexes $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PCy}_3)_2]$ and $[\text{Pt}(\eta^2\text{-norbornene})(\text{PPh}_3)_2]$.^[5]



Scheme 2

In order to probe whether, in the case of an asymmetric TTF derivative such as 3,4-dimethyltetrathiafulvalene (*o*-Me₂TTF), coordination to platinum occurs via the double bond substituted with two hydrogens or, alternatively, via the double bond substituted by the two methyl groups, we also treated $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ with the 3,4-dimethyltetrathiafulvalene. During the reaction, pure yellow $[\text{Pt}(\eta^2\text{-}o\text{-Me}_2\text{TTF})(\text{PPh}_3)_2]$ (**2**) precipitated (Scheme 2). The NMR

spectra indicate the exclusive coordination of the substituted TTF via the $\text{H}-\text{C}=\text{C}-\text{H}$ moiety. Thus, as observed for **1**, the proton NMR spectrum exhibits the signals for the olefinic H atoms centered at $\delta = 3.95$ ($^3J_{\text{P,H}} = 2.4$ Hz and $^3J_{\text{Pt,H}} = 61$ Hz). The resonance of the Me groups appears as a singlet at $\delta = 2.00$. The additional singlets observed at δ 6.30 and 1.96 stemming from 3,4-dimethyltetrathiafulvalene indicate, that as in the case of **1**, an equilibrium occurs in solution between free and complexed 3,4-dimethyltetrathiafulvalene (ratio 1:3.3). Cooling the solution resulted in the progressive increasing of the ratio of complexed to uncomplexed TTF. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is very similar to that of **1** mentioned above, and requires no special comments.

Molecular Structure of **2**

Complex **2** crystallizes, with one solvent molecule (toluene), in the triclinic space group $P\bar{1}$. The molecular structure of the Pt^0 complex is characterized by a trigonal planar ligand arrangement with the alkene in the plane of the triangle (Figure 1). The Pt–P distances [2.293(2) and 2.294(2) Å] lie in the typical range observed in other $[\text{Pt}(\text{olef-})$

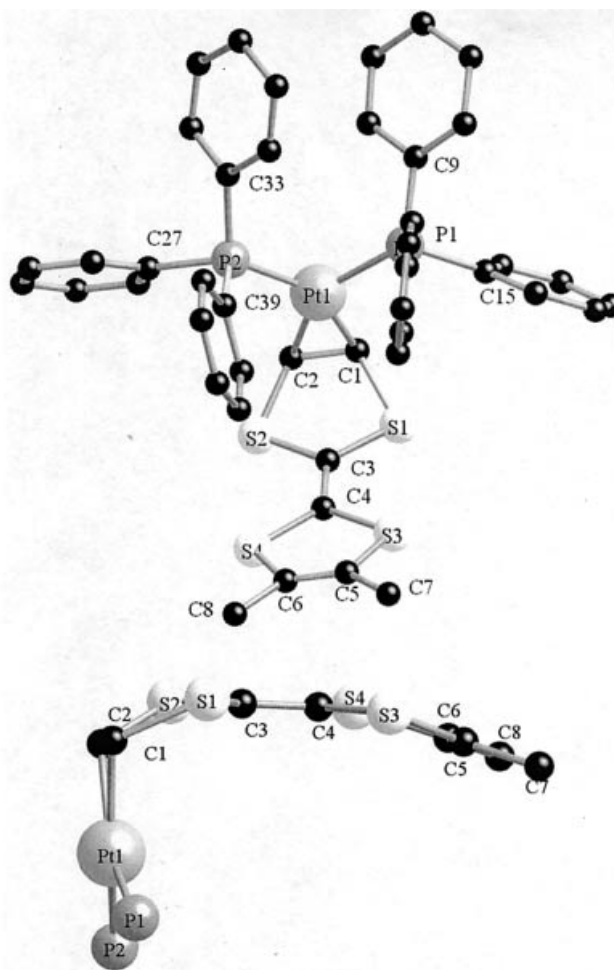


Figure 1. Top: molecular structure of **2** with labelling scheme; bottom: view of the Pt-TTFMe_2 core showing the boat conformation of the TTFs; hydrogen atoms are omitted for clarity

Table 1. Comparison of selected geometric parameters between **2** and [Pt(PPh₃)₂(CH₂=CH₂)]^[7]

Complex	P–Pt–P	Pt–P	C–Pt–C	C(1)–C(2)	Pt–C
2	103.55(8)	2.293(2) 2.294(2)		1.360(11)	2.059 2.007
Pt(PPh ₃) ₂ (CH ₂ =CH ₂)	111.6(1)	2.265(2) 2.270(2)	39.7(4)	1.43(1)	2.11(1) 2.12(1)

in)(PPh₃)₂] complexes.^[6] The P–Pt–P angle [103.55(8)°] is more acute than in the ethylene complex (Table 1). The Pt–C bonds are significantly shorter in **2** in comparison with the starting material [Pt(CH₂=CH₂)(PPh₃)₂]. The TTF part is strongly folded along the S⋯S axis of each fulvalene, with values of 31.02(54)° for S(1)⋯S(2) and 16.52(21)° for S(3)⋯S(4), while the central core [S(1–4), C(3) and C(4)] is nearly planar (Figure 1, bottom). Thus, the boat conformation is much more pronounced in **2** compared with the geometry of the free *o*-Me₂TTF, for which angles of 0.6° and 1.88° have been reported.^[8] These deformations have already been observed with several metal-coordinated TTF derivatives (see for example ref.^[3c]) but not with such magnitude. The increasing of the out-of-plane bend leads to significant changes for the other structural parameters. Table 2 provides a comparison of selected bond lengths and angles

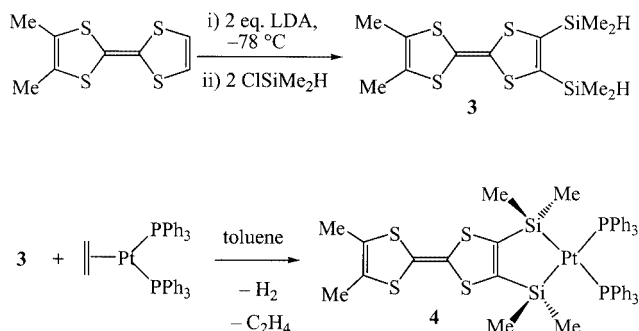
between **2**, and uncoordinated *o*-Me₂TTF. As can be seen, the external C–S bonds become longer upon coordination. This may be due to a reduction of conjugation within the fulvalene rings, which also leads to a shortening of the C(5)–C(6) bond length [1.305(11) vs. 1.338(4) Å]. Conversely, due to the interaction with the platinum, there is a significant lengthening of the C(1)–C(2) bond as observed in almost all cases of coordinated olefins.^[9] In contrast to the symmetrical structure of *o*-Me₂TTF, C(1) and C(2) are not equivalent in **2**: (i) the Pt–C bond lengths are quite different (Table 1), and (ii) the value observed for the S(1)–C(1)–C(2) angle [112.3(6)°] suggests that the C(1) atom approaches a tetrahedral hybridization, whereas the C(1)–C(2)–S(2) angle remains nearly unchanged upon complexation, indicating an sp² hybridization for C(2) [119.9(6)°].

Table 2. Selected bond lengths (Å) and angles (°) for 3,4-dimethyltetrafulvalene,^[8] **2**, and **3**

3,4-Dimethyltetrafulvalene	2	3
S(1)–C(1)	1.743(4)	1.843(8)
S(1)–C(3)	1.765(3)	1.729(9)
S(2)–C(2)	1.739(4)	1.760(9)
S(2)–C(3)	1.767(3)	1.768(8)
C(3)–C(4)	1.340(4)	1.366(10)
C(1)–C(2)	1.308(5)	1.360(11)
S(3)–C(4)	1.753(3)	1.759(9)
S(3)–C(5)	1.755(3)	1.781(9)
S(4)–C(4)	1.762(3)	1.730(10)
S(4)–C(6)	1.758(3)	1.772(8)
C(5)–C(6)	1.338(4)	1.305(11)
C(5)–C(7)	1.500(5)	1.527(10)
C(6)–C(8)	1.503(5)	1.505(12)
C(1)–Si(1)		1.886(2)
C(2)–Si(2)		1.873(3)
C(1)–S(1)–C(3)	94.42(17)	93.4(4)
C(2)–S(2)–C(3)	94.31(17)	91.3(4)
S(1)–C(1)–C(2)	118.2(3)	112.3(6)
C(1)–C(2)–S(2)	118.7(3)	119.9(6)
S(1)–C(3)–S(2)	114.27(17)	114.9(4)
S(2)–C(3)–S(4)	122.9(3)	120.5(7)
C(3)–C(4)–S(3)	123.3(3)	120.9(7)
C(4)–S(4)–C(6)	95.51(15)	95.2(4)
C(4)–S(3)–C(5)	96.14(15)	94.3(4)
S(3)–C(4)–S(4)	113.89(17)	113.9(5)
S(3)–C(5)–C(6)	116.9(2)	117.0(6)
C(6)–C(5)–C(7)	127.0(3)	129.4(8)
S(4)–C(6)–C(5)	117.6(2)	117.2(7)
C(5)–C(6)–C(8)	126.8(3)	128.9(8)
C(2)–C(1)–Si(1)		126.7(3)
C(1)–C(2)–Si(2)		127.5(2)
		128.76(19)

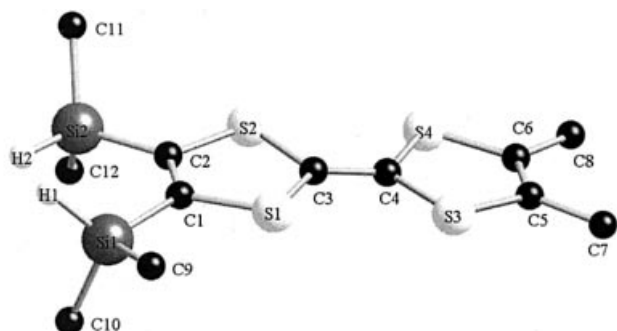
Synthesis and Characterization of a Bis(silylated) Platinum-TTF Complex

One common strategy for the synthesis of substituted TTFs takes advantage of the acidity of the TTF hydrogen atoms.^[10] Indeed, treatment with *n* equivalents of strong bases such as LDA at low temperature affords TTF-Li_{*n*}, which can be treated with a variety of electrophiles. Using this procedure, 3,4-dimethyltetraathiafulvalene was dilithiated with 2 equivalents of LDA, then silylated with chlorodimethylsilane to give 3,4-dimethyl-3',4'-(dimethylsilyl)-tetraathiafulvalene (**3**) (Scheme 3).



Scheme 3

Compound **3** was isolated in 72% yield as orange air-stable solid, soluble in aliphatic hydrocarbons. Recrystallization from a concentrated hexane solution afforded single-crystals suitable for an X-ray diffraction study. The geometry of **3** is shown in Figure 2, structural parameters are given in Table 2. The framework of 3,4-dimethyltetraathiafulvalene is only slightly influenced by the substitution with the dimethylsilyl functions. The geometry around the Si atoms is essentially tetrahedral, with C–Si–C angle values varying between 108.49(17) and 111.5(2)°. The C(1)–Si(1) and C(2)–Si(2) bond lengths [1.886(2) and 1.873(3) Å] are quite similar to that in (TTF)₂SiMe₂ [1.868(5) Å].^[11]

Figure 2. Molecular structure of **3**

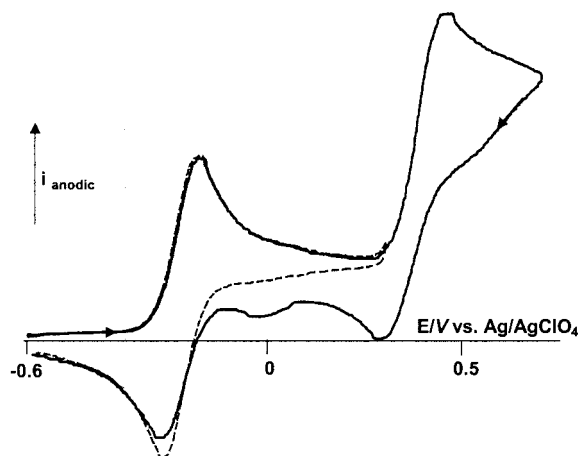
By taking advantage of the reactivity of the Si–H bond towards low valent transition metal centers, compound **3** seemed to be a promising precursor to covalently link a platinum fragment to the TTF unit.^[12] Thus, **3** reacts by oxidative addition with one equivalent of [Pt(η²-

C₂H₄)(PPh₃)₂] in toluene to afford the platinum bis(silyl) complex [Pt{*o*-(Me₂Si)₂TTFMe₂}(PPh₃)₂] (**4**) (Scheme 3). The chelating coordination of the two SiMe₂ groups on each Pt center was confirmed by the ¹H NMR spectrum [singlet, δ = –0.13 ppm, ³J(Pt–H) = 22.1 Hz], and the ³¹P{¹H} NMR spectrum [δ = 30.0 ppm, ¹J(Pt–P) = 1716 Hz].

Cyclic voltammetric data for *o*-Me₂TTF, **3**, and **4** are given in Table 3. In each case, two reversible or quasi reversible single-electron oxidation waves were observed corresponding to the oxidation of the TTF core (Figure 3). Substitution of the olefinic hydrogens in *o*-Me₂TTF by the SiMe₂H group induces a slight cathodic shift for the first oxidation wave due to the inductive effect of the methyl group, whereas *E*₂^{1/2} remains unchanged. More interesting is the fact that the bis(silyl) complex **4** shows a strong cathodic shift (nearly 0.2 V) for the two redox processes. This observation is contrary to the tendency reported in the case of TTFs functionalized with phosphane or pyridine. The latter always display shifts towards more anodic potentials upon coordination.^[3e,3j] This implies a strong interaction between the TTF core and the metallic fragment. Note also that the second oxidation wave in **4** appears not totally reversible at standard scan rates (50–250 mV s^{–1}), since an additional reduction peak was observed at *E*_{pc} ≈ 0 V. This peak disappeared when the scan rate was faster (= 1 V s^{–1}) or when the potential was reversed just before the second oxidation wave (Figure 3). Nevertheless the potential, and the reversibility of the first electron transfer offer the possibility of synthesizing open shell species from this organometallic complex.

Table 3. Voltammetric data (*E* in V vs. Ag/0.1 M AgClO₄)

Compound	<i>E</i> ₁ ^{1/2}	<i>E</i> ₂ ^{1/2}
DMTTF	+ 0.05	+ 0.53
3	–0.01	+ 0.53
4	–0.24	+ 0.34

Figure 3. Cyclic voltammograms of **4** in CH₂Cl₂ solution on a platinum electrode; scan rate: 100 mV s^{–1}

Conclusion

In summary, the bonding modes between tetrathiafulvalenes and transition metal centers described in this paper highlight the possible development of novel classes of TTF derivatives using strategies from organometallic chemistry. For example, insertion of unsaturated organic substrates such as alkynes into the platinum-silicon bond may be an original tool for introducing functionalization to the TTF core.^[13] On the other hand, the reactivity of the Si–H bond is not restricted to platinum, and generalization to other metal centers may provide a family of transition metal–silicon complexes in which the redox properties of the TTF may be fine-tuned by the metallic fragment. Both approaches, as well as potential applications in materials science, are currently being pursued in our laboratories.

Experimental Section

General Comments: All reactions were performed under dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods, freshly distilled, and saturated with nitrogen prior to use. TTF,^[14] *o*-Me₂TTF,^[15] and [Pt(PPh₃)₂(C₂H₄)]^[16] were prepared according to published procedures. The ¹H, ³¹P{¹H}, and ¹⁹⁵Pt NMR spectra were recorded at 300.13, 81.01, and 42.95 MHz, respectively, on a Bruker Avance 300 instrument. ¹⁹⁵Pt chemical shifts were externally referenced to aqueous K₂PtCl₄ with down-field chemical shifts reported as positive. Elemental analyses were performed at the Université de Bourgogne with an EA 1108 Fisons instrument.

Electrochemical Measurements: Voltammetric analyses were carried out, at ambient temperature, in a standard three-electrode cell with a Radiometer PGP 201 potentiostat. The electrolyte consisted of a 0.2 M *n*Bu₄NPF₆ solution in CH₂Cl₂. The working electrode was a platinum disk electrode, and the auxiliary electrode was a platinum wire. The reference electrode was a silver/silver ion electrode, Ag/Ag⁺ (0.1 M AgClO₄ in acetonitrile) separated from the solution by a sintered glass disk. After each measurement the reference was checked against the ferrocene-ferrocenium couple (+ 0.16V relative to this reference electrode).

Synthesis of [Pt(η²-TTF)(PPh₃)₂] (1): To a solution of [Pt(η²-C₂H₄)(PPh₃)₂] (375 mg, 0.5 mmol) in toluene (8 mL) was added TTF (110 mg, 0.54 mmol). The solution was stirred at room temperature for 1 h. Hexane was then added and the resultant solution cooled to 4 °C. The solid, which formed, was collected by filtration, washed with hexane and dried to provide **1** as an orange solid. (393 mg, 85% yield). ¹H NMR (CDCl₃): δ = 3.96 (t br., 2 H, H-TTF, ³J_{H,P} = 2.5, ²J_{H,Pt} = 60.2 Hz), 6.32 (s, 2 H, H-TTF) 7.14–7.24 (m, 30 H, Ph). ³¹P{¹H} NMR: δ = 27.85 (s, ¹J_{Pt,P} = 3444 Hz) ppm. C₄₂H₃₄P₂PtS₄ (924.00): calcd. C 54.60, H 3.71; found C 55.01, H 3.60.

Synthesis of [Pt(η²-*o*-Me₂TTF)(PPh₃)₂] (2): To a solution of [Pt(η²-C₂H₄)(PPh₃)₂] (337 mg, 0.45 mmol) in toluene (8 mL) was added *o*-Me₂TTF (116 mg, 0.5 mmol). The solution was stirred at room temperature for 0.5 h. The orange complex precipitated gradually from solution. After cooling at 4 °C the supernatant liquid was decanted, and the residue washed with hexane. (381 mg, 89% yield). ¹H NMR (CDCl₃): δ = 2.00 (s, 6 H, CH₃), 3.95 (t br., 2 H, H-TTF, ³J_{H,P} = 2.4, ²J_{H,Pt} = 61.0 Hz), 7.16–7.24 (m, 30 H, Ph)

ppm. ³¹P{¹H} NMR: δ = 27.8 (s, ¹J_{Pt,P} = 3450 Hz) ppm. ¹⁹⁵Pt{¹H} NMR: δ = –3206 (t, ¹J_{Pt,P} = 3450 Hz) ppm. C₄₄H₃₈P₂PtS₄ (952.05): calcd. C 55.51, H 4.02; found C 55.86, H, 4.17.

Synthesis of 3,4-Dimethyl-3',4'-(dimethylsilyl)tetrathiafulvalene (3): A solution of *o*-Me₂TTF (0.23 g, 1 mmol) in THF (20 mL) was treated at –78 °C with LDA (2.5 mmol). The yellow precipitate was stirred at –78 °C for 4 h, and then treated with chlorodimethylsilane (2.6 mmol). The reaction temperature was allowed to rise slowly overnight to room temperature. The solvent was then removed under reduced pressure, and the residue was extracted with diethyl ether. After evaporation of the diethyl ether, the resultant solid was recrystallized from hexane to give **3** as orange crystals (250 mg, 72% yield). ¹H NMR (CDCl₃): δ = 0.34 (d, 12 H, SiMe₂, ³J_{H,H} = 3.8 Hz), 1.94 (s, 6 H, Me-TTF), 4.49 (h, 2 H, Si–H) ppm. IR (KBr): ν̄ = 2163 (Si–H) cm^{–1}. C₁₂H₂₀S₄Si₂ (348.70): calcd. C 41.33, H 5.78; found C 41.45, H 5.75.

Synthesis of [Pt{*o*-(Me₂Si)₂TTFMe₂}(PPh₃)₂] (4): To a solution of 3,4-dimethyl-3',4'-(dimethylsilyl)tetrathiafulvalene (**3**) (105 mg, 0.3 mmol) in toluene (7 mL) was added [Pt(η²-C₂H₄)(PPh₃)₂] (210 mg, 0.28 mmol) in toluene (7 mL). The resultant orange solution was stirred at room temperature for 2 h. The yellow complex precipitated gradually from solution. The supernatant liquid was decanted and the residue was washed with hexane (224 mg, 75% yield). ¹H NMR (CDCl₃): δ = –0.13 (s, 12 H, SiMe₂, ²J_{Pt,H} = 22.1 Hz), 1.91 (s, 6 H, Me-TTF), 7.16–7.30 (m, 30 H, Ph) ppm. ³¹P{¹H} NMR: δ = 30.0 (s, ¹J_{Pt,P} = 1716 Hz) ppm. C₄₈H₄₈P₂PtS₄Si₂ (1066.35) calcd. C 54.07, H 4.54; found C 54.40, H 4.65.

Table 4. X-ray structural data for **2** and **3**

Compound	2	3
Formula	C _{47.5} H ₄₂ P ₂ PtS ₄	C ₁₂ H ₂₀ S ₄ Si ₂
Fw	998.08	348.70
Crystal size (mm)	0.32 × 0.15 × 0.08	0.77 × 0.37 × 0.19
<i>T</i> (K)	293(2)	293 (2)
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.4534(19)	5.7661(12)
<i>b</i> (Å)	14.305(3)	9.1180(18)
<i>c</i> (Å)	16.968(3)	18.653(4)
<i>α</i> (deg)	90.33(3)	89.05(3)
<i>β</i> (deg)	101.71(3)	95.87(3)
<i>γ</i> (deg)	108.89(3)	107.54(3)
<i>V</i> (Å ³)	2119.4(7)	930.1(3)
<i>Z</i>	2	2
ρ _{calcd.} (g cm ^{–3})	1.564	1.245
μ (mm ^{–1})	3.616	0.623
<i>F</i> (000)	998	368
λ (Å)	0.71073	0.71073
θ range, deg	1.87–25.79	2.34–25.84
Index ranges	–11 ≤ <i>h</i> ≤ 11, –17 ≤ <i>k</i> ≤ 17, 0 ≤ <i>l</i> ≤ 20	–7 ≤ <i>h</i> ≤ 6, –11 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 22
No. of reflns. collected	7577	3298
No. of ind. reflns.	4162	2248
Largest diff. peak and hole, e(Å ^{–3})	–1.050/1.258	–0.177/0.268
Final <i>R</i> indices ^[a]	0.0446	0.0397
<i>R</i> indices (all data)	0.1030	0.0609
GOF on <i>F</i> ²	0.749	0.990

^[a] *R*(*F*) = Σ||*F*_o| – |*F*_c|| / Σ|*F*_o|.

Crystallographic Data Collection and Structure Determinations of 2 and 3: Suitable crystals of **2** and **3** for X-ray diffraction were obtained by crystallization from toluene and hexane, respectively. A single-crystal of each compound was mounted in a glass capillary using Araldite glue. Data were collected with a Stoe-IPDS diffractometer, with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å). Details are given in Table 4. A numerical absorption correction was applied (FACEIT, Stoe). The structures were solved by direct methods, and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-H atoms. H atoms were included in calculated positions, and constrained to ride on the parent C atoms. All calculations were performed with the SHELTX package.^[17] CCDC-226740 for [Pt(PPh₃)₂](*o*-Me₂TTF)] and -226741 for [*o*-Me₂TTF(SiMe₂H)₂] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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