Synthesis and some properties of bis- and tetrakis(triphenylstannyl) tetrathiafulvalenes and tetraiodotetrathiafulvalene

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Abstract

Bis- and tetrakis(triphenylstannyl)tetrathiafulvalenes were prepared from the corresponding lithio-derivatives and chlorotriphenyltin, and their structures were determined by X-ray analysis. Their absorption maxima in the electronic spectrum showed a bathochromic shift. Their redox potentials shifted only a little to a lower region. The charge-transfer complex of the tetra-substituted derivative with TCNQ was isolated. Bis(trimethylstannyl)tetrathiafulvalene did not react with $(\eta\text{-Cp})(CO)_2FeI$ and the reaction with $(COD)PtCl_2$, followed by addition of tributylphosphine, gave a complex mixture, from which $(C_2H_2S_2)Pt(PBu_3)_2$ was isolated in a low yield. The structure was confirmed by X-ray diffraction. A convenient preparation of tetrathiafulvalene and tetraiodotetrathiafulvalene is also reported. © 1997 Elsevier Science S.A.

Keywords: Sn; X-ray diffraction; Charge-transfer complex

1. Introduction

Tetrathiafulvalene (TTF) (1) is a unique and electron-rich unsaturated compound and its charge-transfer complex is a candidate for functionalized compounds [1]. Many heteroatom-substituted derivatives were investigated [2] but few were reported concerning metal-substituted TTF [3], although oligolithio- [4,5] and mono(trimethylstannyl)tetrathiafulvalene were prepared as synthetic intermediates [6]. The enhancement of the electron density on the TTF system may induce the increase of its functionality. We here report the preparation and some properties of bis- (2a) and tetrakis(triphenylstannyl)tetrathiafulvalenes (3) and the related compounds.

2. Results and discussion

Compound (1) was lithiated with 4 equiv. of LDA [5], followed by addition of chlorotriphenyltin, and chromatographic separation on deactivated Al_2O_3 to

give bis(triphenylstannyl)tetrathiafulvalene (2a) in 57% yield. Similarly, the lithiated TTF was treated with 2.5 equiv. of chlorotrimethyltin and chlorotributyltin (see Scheme 1) to afford bis(trimethylstannyl)- (2b) and bis(tributylstannyl)tetrathiafulvalenes (2c) containing mono-substituted derivative, respectively, but the complete separation and identification of them were impossible because of their instability towards Al_2O_3, although they were assigned by their ^1H NMR spectra. Attempted separation by the sublimation method of the mixture was unsuccessful because of the instability of the components on heating. The tetralithiated TTF, which was prepared from 1 and 10 equiv. of LDA [5], was treated with chlorotriphenyltin, followed by chromatography on deactivated Al_2O_3, to give tetrakis(triphenylstannyl)tetrathiafulvalene (3) in 30% yield (Scheme 1). The Raman spectra of 2a and 3 showed the C=C stretching vibration at $1496\,cm^{-1}$ and $1533\,cm^{-1}$ respectively. In the ^{13}C NMR spectrum of 3, the central olefinic carbons resonated at δ 112.04 accompanied with a satellite ($^3J_{C,Sn} = 32.2\,Hz$) and the other fulvalene carbons at δ 139.12 with satellites, $^1J_{C,Sn} = 434.9$ and $316.8\,Hz$. Also, the ^{13}C NMR spectrum of 2a showed the central olefinic carbons resonated at

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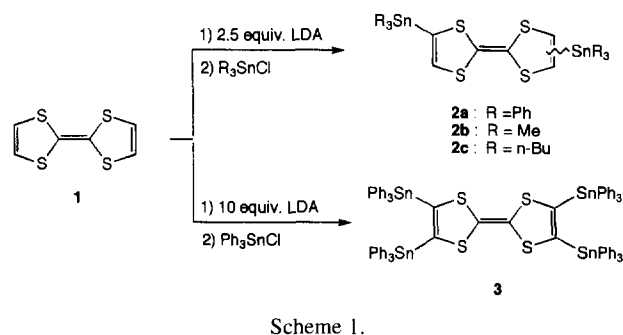
Scheme 1.

δ 111.70 and 111.85 and the other olefinic carbons at δ 127.05 and 126.99 ($^2J_{C,Sn}$ = 33.5 Hz) and 130.87. In the ^1H NMR spectrum of **2a**, the olefinic proton was observed at δ 6.28 (s, 2H, $^3J_{H,Sn}$ = 44.2 and 35.8 Hz) and the phenyl protons at δ 7.30–7.71 (m, 30H).

A single crystal of **3** was obtained by the recrystallization from pentane–carbon disulfide and the X-ray diffraction analysis was performed. The ORTEP view of **3** is shown in Fig. 1 and the crystallographic data are summarized in Table 1. The selected bond distances and angles are shown in Table 2. The crystals of **3** contained 1 equiv. of benzene. Half of the molecule is crystallographically unique, with the molecule located on an
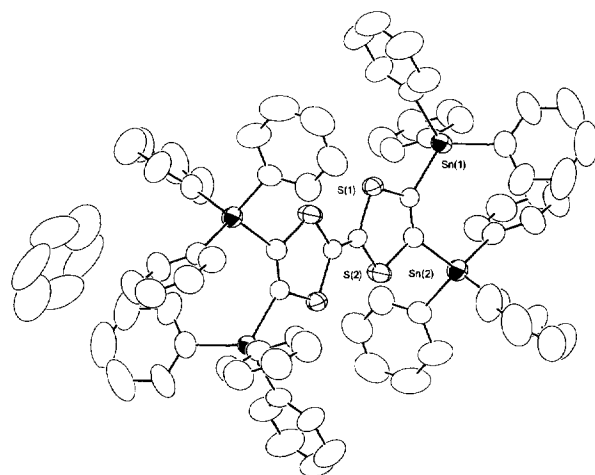
Fig. 1. ORTEP view of complex **3**.

inversion center. The framework of TTF is only a little influenced on the substitution by the triphenylstannyl group. That is, the central C=C bond of **3** [1.329(10) Å] is somewhat shorter than that of **1** [1.349(3) Å] and the terminal C=C bond [1.350(10) Å] is a little longer than that of **1** [1.314(3) Å] [7]. The S–C–S angle in **3** [112.5(4)°] is smaller than that of **1** [114.5°]. A similar

Table 1
Crystallographic data for complexes **3**, **2a**, and **5**

	3	2a	5
Molecular formula	$C_{78}H_{60}S_4Sn_4$	$C_{42}H_{32}S_4Sn_2$	$C_{26}H_{56}S_2P_2Pt$
Molecular wt.	1600.35	902.34	689.89
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/a$ (#14)	$P1$ (#1)	$P2_12_12_1$ (#19)
a (Å)	18.512(6)	6.526(2)	9.442(3)
b (Å)	11.434(4)	9.815(6)	16.626(4)
c (Å)	19.13(1)	16.821(6)	21.724(8)
α (deg)		87.2(1)	
β (deg)	109.15(2)	87.21(8)	
γ (deg)		71.13(7)	
V (Å^3)	1073.74	961.26	3410.29
Z	2	1	4
D_{cal} (g cm^{-3})	1.39	1.47	1.34
Crystal dimensions (mm^3)	0.40 × 0.40 × 0.05	0.20 × 0.20 × 0.04	0.26 × 0.26 × 0.22
Linear abs coeff. (cm^{-1})	14.376	14.551	43.757
Radiation (λ (Å))	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
$2\theta_{max}$ (deg)	61	61	61
Reflection (hkl) limits	$0 < h < 21, 0 < k < 16,$ $-27 < l < 25$	$0 < h < 8, -12 < k < 13,$ $-23 < l < 23$	$0 < h < 13, 0 < k < 22,$ $0 < l < 30$
Total no. of rflns measured	9647	4445	5493
No. of unique rflns	9277	4445	5466
No. of rflns used in L.S.	6098	2101	3281
L.S. parameters	415	427	336
R	0.047	0.131	0.041
R_w	0.054	0.164	0.042
Max peak in final Fourier map (e$^-$ Å^{-3})	0.74	4.62	0.53
Min peak in final Fourier map (e$^-$ Å^{-3})	−0.85	−4.55	−0.79

Table 2
Selected bond distances (Å) and angles (deg) for **3**

Bond distances			
Sn(1)–C(2)	2.152(7)	Sn(2)–C(3)	2.157(7)
S(1)–C(1)	1.767(7)	S(1)–C(2)	1.756(7)
S(2)–C(1)	1.747(7)	S(2)–C(3)	1.763(7)
C(1)–C(1)	1.329(10)	C(2)–C(3)	1.350(10)
Angles			
C(1)–S(1)–C(2)	96.8(4)	C(1)–S(2)–C(3)	97.2(4)
S(1)–C(1)–S(2)	112.5(4)	S(1)–C(1)–C(1)	123.0(6)
S(2)–C(1)–C(1)	124.5(6)	Sn(1)–C(2)–S(1)	113.2(4)
Sn(1)–C(2)–C(3)	130.0(5)	S(1)–C(2)–C(3)	116.8(5)
Sn(2)–C(3)–S(2)	110.3(4)	Sn(2)–C(3)–C(2)	133.0(5)
S(2)–C(3)–C(2)	116.3(5)		

tendency was also observed in tetrakis(trifluoromethyl)tetrathiafulvalene [8] and bis(tetrathiafulvalenyl)dimethylsilane [9]. A single crystal X-ray diffraction analysis of **2a** was also performed but a sufficient *R* value could be not obtained (*R* = 0.12) because of the lack of a good single crystal of **2a**. The crystallographic data and the ORTEP view of **2a** are shown in Table 1 and Fig. 2 respectively. As seen clearly from the ORTEP view, complex **2a** adopts the trans configuration of the triphenylstannyl group. This is probably due to a less solubility of the trans isomer on the recrystallization, because the ^{1}H NMR spectrum of the reaction product showed the formation of a mixture of trans and cis isomers.

Two absorption maxima observed in the electronic spectra of the bis- (**2a**) (319 and 386 nm) and tetrakis(triphenylstannyl)-substituted derivatives (**3**) (332.5 and 419.5 nm) showed a bathochromic shift compared with those in the unsubstituted TTF (310.5 and 366 nm). The bathochromic shift is probably due to the electron-donating ability of the triphenylstannyl group [10]. This is also supported by the oxidation potentials of complexes **2a** and **3**. The cyclic voltammograms of **2a** and **3** were measured in 0.1 M solution of (*n*-Bu)$_4$NClO$_4$ in CH$_2$Cl$_2$ [10] (the redox potential of TTF has been measured, see Ref. [11]) and two quasi-reversible waves were observed in both derivatives. The first redox potential of **2a** (−0.15 V) is closely similar to that of **1** (−0.12 V), but the second redox potential
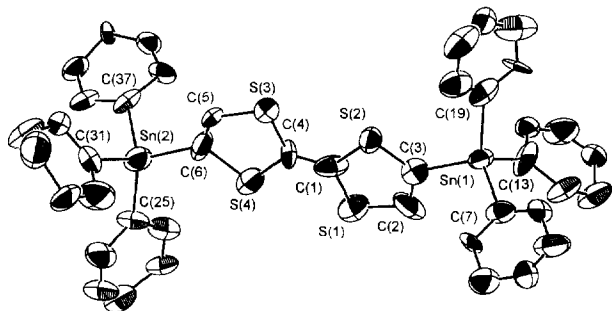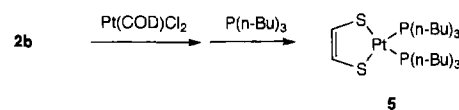

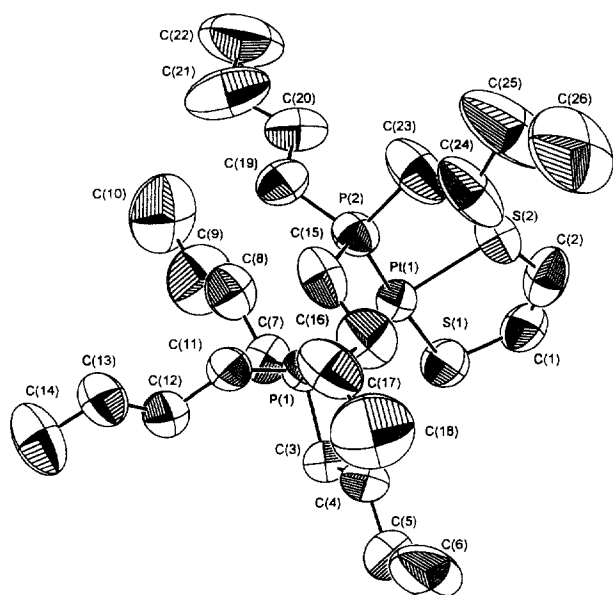Fig. 2. ORTEP view of complex **2a**.

Pt(COD)Cl$_2$ → P(n-Bu)$_3$ →

Scheme 2.

(+0.32 V) shifted considerably to a higher potential than that of **1** (+0.22 V) [11]. On the other hand, the first redox potential of **3** (−0.27 V) shifted by 0.15 V to a lower potential compared with that of **1** and the second redox potential (0.22 V) remained nearly unchanged. The low-potential shift of the first redox potential seems to reflect that the triphenylstannyl group functions as a weakly electron-donating substituent toward the TTF system. The differences ($\Delta E_{1/2}$) between the first and second redox potentials of **2a** and **3** are nearly identical to each other (0.47 V for **2a** and 0.45 V for **3**), suggesting likely a similar stability of the radical cation [12]. The reaction of either **2a** or **3** with tetracyanoquinodimethane (TCNQ) in CH$_2$Cl$_2$ exhibited the formation of the charge-transfer complex whose CT-absorption band appeared at 852 nm [10] (TTF forms the charge-transfer complex with TCNQ, see Ref. [13]). However, the color of the solution of **3** and 1.5 equiv. of TCNQ was dark green, but the solution of **2a**–TCNQ showed only a faint greenish color. In coincidence with this observation, the charge-transfer complex of **3** with TCNQ was obtained as black crystals, while no similar complex was isolated from the reaction of **2a** with TCNQ. This fact may be elucidated as follows. The bis(triphenylstannyl)-substituted derivative (**2a**) has the redox potential similar to TTF and a large steric hindrance of the triphenylstannyl group. The latter effect would disturb the formation of the stable charge-transfer complex by unfavorable overlapping of the TTF with TCNQ. In the tetra-substituted derivative (**3**), the considerably lower first redox potential may overcome the instability of the charge-transfer complex by the steric hindrance. The charge-transfer complex (**4**) showed the CN stretching vibration at 2190 cm^{-1} which was shifted by 14 cm^{-1} to lower wavenumber than that of TTF · TCNQ (2204 cm^{-1}), in which the lower-wavenumber shift of 22 cm^{-1} from the corresponding band of TCNQ was observed.

The palladium-catalyzed cross-coupling reaction [14] of bis(trimethylstannyl)tetrathiafulvalene (**2b**) with (η-Cp)(CO)$_2$FeI was attempted unsuccessfully. ^{1} No reaction took place in the presence of a catalytic amount of [PdCl$_2$(MeCN)$_2$] [16] and the reaction using Pd(PPh$_3$)$_4$ [17] as a catalyst gave only (η-Cp)(CO)(Ph$_3$P)FeI. The reaction of **2b** with Pt(COD)Cl$_2$ afforded an intractable black solid, followed by the treatment with tributylphos-

^{1} The cross-coupling reaction of trimethylstannylacetylide with FpI has been reported, see Ref. [15].

Fig. 3. ORTEP view of complex 5.

Table 3
Selected bond distances (Å) and angles (deg) for 5

Bond distances			
Pt(1)–S(1)	2.314(5)	Pt(1)–S(2)	2.308(5)
Pt(1)–P(1)	2.285(4)	Pt(1)–P(2)	2.288(5)
S(1)–C(1)	1.677(17)	S(2)–C(2)	1.777(19)
C(1)–C(2)	1.30(3)		
Angles			
S(1)–Pt(1)–S(2)	87.5(2)	S(1)–Pt(1)–P(1)	85.1(2)
S(2)–Pt(1)–P(2)	88.4(2)	P(1)–Pt(1)–P(2)	99.0(2)
Pt(1)–S(1)–C(1)	105.3(6)	Pt(1)–S(2)–C(2)	100.6(7)
S(1)–C(1)–C(2)	120.9(14)	S(2)–C(2)–C(1)	125.6(14)

phine, to give pale yellow crystals in a tiny yield. The ^{1}H NMR spectrum of the product (5) (Scheme 2) showed an olefinic proton at δ 6.66 (d, $J = 4.1$ Hz) with a satellite of ^{195}Pt ($J = 76.9$ Hz) and the signals due to a butyl group at δ 0.93 (t), 1.40–1.56 (m), and 2.01–2.05 (m). In the ^{13}C NMR spectrum, one olefinic carbon appeared at δ 126.41 and four carbon signals assigned to the butyl group resonated at δ 13.72, 24.16, 25.48, and 26.20. Because it was difficult to assign the structure of 5 definitely from these spectral data alone, the X-ray single crystal diffraction experiment was carried out. The crystallographic data of 5 are summarized in Table 1 and the ORTEP view was shown in Fig. 3. The selected bond distances and angles are shown in Table 3. As seen clearly in Fig. 3, complex 5 is the bis(phosphine) Pt(II) complex of dithiolene. Other asymmetrical bis(phosphine) dithiolene analogs have been reported only a little [18,19]. The Pt–S distances [2.314(5) and 2.308(5) Å] in 5 are similar to those in the related complexes, Pt(dmit)(dppe) (6), [2.315(3) and 2.308(3) Å] [20] and somewhat longer than those of PtS$_4$C$_4$Ph$_4$ (7) [2.246 and 2.244 Å] [21], probably because of a trans influence of the phosphine ligand. The Pt–P distances [2.285(4) and 2.288(5) Å] in 5 are comparable to those in 6 [2.251(3) and 2.258(3) Å]. The S–Pt–S angle [87.5(2)°] in 5 is close to that of 7 [87.6°] and somewhat smaller than that in 6 [90.0(1)°] and the P–Pt–P angle [99.0(2)°] in 5 is considerably larger than that in 6

[85.2(1)°], probably reflecting that the Pt(II) atom and the P atoms in 6 are incorporated in the five-membered chelate-ring.

Finally, tetraiodotetrathiafulvalene (8) was recently reported to be prepared by the reaction of diiodo-1,3-dithiole-2-one with triethylphospite [22]. The tetraiodo derivative could be obtained conveniently in 26% yield, along with diiodotetrathiafulvalene (9) (11%), by the lithiation of TTF with 10 equiv. of LDA, followed by the addition of iodine at low temperature (Scheme 3). On the other hand, Becker et al. [23] reported that tetraiodotetrathiafulvalene was not synthesized in the similar conditions using 5 equiv. of LDA, although tetrabromo- and tetrachlorotetrathiafulvalene were obtained. However, the use of 12 equiv. of LDA did not improve the yield of the tetraiodo derivative (25%).

3. Experimental

3.1. General

All reactions were carried out under a nitrogen atmosphere and the work-up was carried out in air. Solvents were dried by standard procedures. IR spectra were recorded as KBr pellets on a Perkin–Elmer System 2000 spectrometer. NMR spectra were recorded on a Bruker AM400 or ARX400 instrument, using TMS as an internal standard. Electrochemical measurements were by cyclic voltammetry in a solution of 0.1 M (n-Bu)$_4$NClO$_4$ in acetonitrile under nitrogen at 25 °C, using a standard three-electrode cell on a BAS CV-27 analyzer. All potentials referenced to FcH/FcH$^+$, which had a potential of $+0.14$ V vs. Ag/AgNO$_3$ in this medium. The scan rate was 100 mV s^{-1}. TTF was prepared by the modified Yoshida procedure [24] from the
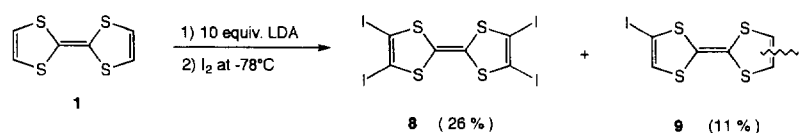
Scheme 3.

tetraester (vide infra). All the other chemicals were reagent grade.

3.2. Procedure

3.2.1. TTF

A solution of tetra(carbomethoxy)tetrathiafulvalene (0.44 g, 1 mmol) and LiCl · H$_2$O (0.17 g, 4 mmol) in DMF (10 ml) was heated on an oil bath at 170 °C for 2.5 h. The solution was poured into water and the mixture was extracted with CH$_2$Cl$_2$. The extract was washed with water and dried over MgSO$_4$. After evaporation, the residue was chromatographed on SiO$_2$ with elution of hexane and then CH$_2$Cl$_2$ to give TTF (0.10 g, 50% yield) and bis(carbomethoxy)tetrathiafulvalene (34 mg, 10%).

From the similar reaction of bis(carbomethoxy)tetrathiafulvalene using 2 equiv. of lithium chloride monohydrate, TTF was obtained in 64–73% yield.

3.2.2. Bis(triphenylstannyl)tetrathiafulvalene (2a)

To the solution of LDA, prepared from n-BuLi (2.5 ml, 40 mmol) and (i-Pr)$_2$NH (0.56 ml, 4 mmol) in THF (5 ml) at −78 °C, was added a solution of TTF (0.18 g, 0.88 mmol) in THF (10 ml). The solution was stirred for 1 h at the temperature and then Ph$_3$SnCl (1.54 g, 4.0 mmol) was added to the solution. After stirring for 30 min, the solution was warmed slowly to room temperature. The solvent was evaporated and then the residue was chromatographed on deactivated Al$_2$O$_3$ (Brockmann's activity IV) by elution of hexane–CH$_2$Cl$_2$. The yellow crystals obtained were recrystallized from CH$_2$Cl$_2$–pentane to give pure 2a (0.45 g, 57%). M.p. 208–210 °C. Anal. Found: C, 55.97; H, 3.55%. C$_{42}$H$_{32}$S$_4$Sn$_2$ calc.: C, 55.90; H, 3.57%. IR (KBr): 1481 cm^{-1} (C=C). Raman: 1496 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.28 ($^3J_{Sn,H}$ = 44.2 and 35.8 Hz, 2H, C–H) and 7.30–7.71 (m, 30H, Ph). ^{13}C NMR (100 MHz, CDCl$_3$): δ 111.70 and 111.85 (C=C), 127.05 and 126.99 ($^2J_{Sn,C}$ = 33.5 Hz, CH), 128.93 ($^2J_{Sn,C}$ = 55.8 Hz, o-Ph), 129.74 ($^4J_{Sn,C}$ = 11.9 Hz, p-Ph), 130.84 and 130.95 (Sn–C=), 136.07 ($^1J_{Sn,C}$ = 577.9 and 551.4 Hz, ipso-Ph), and 136.94 (d, $^3J_{Sn,C}$ = 40.6 Hz, m-Ph). UV–vis (CH$_2$Cl$_2$): 319 (log ε 4.20) and 386 nm (3.26).

3.2.3. Tetrakis(triphenylstannyl)tetrathiafulvalene (3)

To the solution of LDA, prepared from n-BuLi (6.3 ml, 10 mmol) and (i-Pr)$_2$NH (1.4 ml, 10 mmol) in THF (5 ml) at −78 °C, was added a solution of TTF (0.19 g, 0.94 mmol) in THF (10 ml). After the solution had been stirred for 2 h at the temperature, Ph$_3$SnCl (3.85 g, 10.0 mmol) was added to the solution at −90 °C. The solution was stirred for 30 min and then the solution was warmed slowly to room temperature. After evaporation, the residue was chromatographed on deac-

tivated Al$_2$O$_3$ (activity III) by elution of hexane–CH$_2$Cl$_2$. The crystals obtained were recrystallized from CH$_2$Cl$_2$–pentane to give 3 as deep yellow crystals (0.44 g, 30%). M.p. 226 °C. Anal. Found: C, 58.65; H, 3.74%. C$_{78}$H$_{60}$S$_4$Sn$_4$ calc.: C, 58.54; H, 3.78%. IR (KBr): 1430 cm^{-1} (C=C). Raman: 1000, 1580, and 3044 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.08–7.31 (m, 60H, Ph). ^{13}C NMR (100 MHz, CDCl$_3$): δ 112.04 ($^3J_{Sn,C}$ = 32.2 Hz, C=C), 128.45 ($^2J_{Sn,C}$ = 55.4 Hz, o-Ph), 129.09 ($^4J_{Sn,C}$ = 12.1 Hz, p-Ph), 136.91 ($^3J_{Sn,C}$ = 40.3 Hz, m-Ph), 137.49 ($^1J_{Sn,C}$ = 565.8 and 541.7 Hz, ipso-Ph), and 139.12 ($^1J_{Sn,C}$ = 434.9 and 316.8 Hz, Sn–C=). UV–vis (CH$_2$Cl$_2$): 332 (log ε 4.26) and 419 nm (3.39).

3.2.4. Bis(trimethylstannyl)tetrathiafulvalene (2b)

According to the procedure similar to that of 2a, using chlorotrimethyltin (0.80 g, 4.0 mmol) and deactivated Al$_2$O$_3$ (activity V) instead of chlorotriphenyltin and deactivated Al$_2$O$_3$ (activity IV), 2b was isolated as a yellow oil containing a small amount (ca. 20%) of monosubstituted TTF in ca. 75% yield (by NMR). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.33 ($^2J_{Sn,H}$ = 56.8 Hz, Me), 6.12 ($^3J_{Sn,H}$ = 32.5 Hz, C–H of cis-isomer) and 6.13 ($^3J_{Sn,H}$ = 32.5 Hz, C–H of trans-isomer). ^{13}C NMR (100 MHz, CDCl$_3$): δ −8.41 ($^1J_{Sn,C}$ = 373.2 and 356.6 Hz), 111.65 (C=C, $^3J_{Sn,C}$ = 28.2 Hz), 122.85 ($^2J_{Sn,C}$ = 29.1 Hz, CH of trans-isomer), 122.75 ($^2J_{Sn,C}$ = 28.6 Hz, CH of cis-isomer), 134.18 ($^1J_{Sn,C}$ = 298.7 Hz Sn–C of trans-isomer), and 134.32 (Sn–C of cis-isomer). The assignment of cis- and trans-isomers may be inverse.

3.2.5. Bis(tributylstannyl)tetrathiafulvalene (2c)

According to the procedure similar to that of 2a, using chlorotributyltin (1.08 ml, 4.0 mmol) and deactivated Al$_2$O$_3$ (activity V) instead of chlorotriphenyltin and deactivated Al$_2$O$_3$ (activity IV), 2c was isolated as a yellow oil containing a small amount (ca. 10%) of mono-substituted TTF in ca. 60% yield (by NMR). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.90 (t, Me), 1.04–1.60 (m, CH$_2$), 6.08 ($^3J_{Sn,H}$ = 28.4 Hz, C–H of cis-isomer) and 6.09 ($^3J_{Sn,H}$ = 28.4 Hz, C–H of trans-isomer). ^{13}C NMR (50 MHz, CDCl$_3$): δ 10.76 ($^1J_{Sn,C}$ = 353.0 and 337.3 Hz, α-CH$_2$, cis), 11.73 ($^1J_{Sn,C}$ = 345.4 and 330.1 Hz, α-CH$_2$, trans), 13.40 (Me), 27.04 ($^2J_{Sn,C}$ = 58.7 Hz, β-CH$_2$, cis), 27.11 ($^2J_{Sn,C}$ = 64.3 Hz, β-CH$_2$, trans), 28.68 ($^3J_{Sn,C}$ = 21.3 Hz, γ-CH$_2$, cis), 28.77 ($^3J_{Sn,C}$ = 19.3 Hz, γ-CH$_2$, trans), 110.76 and 111.18 (C=C, cis and trans), 122.30 and 122.70 (Sn–C=, cis and trans), and 133.58 (Sn–C, cis and trans). The assignment of cis- and trans-isomers may be inverse.

3.2.6. [TTF(SnPh$_3$)$_4$][TCNQ] (4)

A solution of 3 (87.2 mg, 0.05 mmol) and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) (10.2 mg, 0.05 mmol)

in chlorobenzene (5 ml) was gently refluxed for 1 h. The solution was cooled to room temperature to give **4** (18 mg. 20%) as black crystals, which were recrystallized from chlorobenzene to give the title complex as black needles. M.p. ca. 135 °C (dec.). Anal. Found: C, 59.99; H, 3.41%. $C_{90}H_{64}N_4S_4Sn_4$ calc.: C, 59.90; H, 3.57%. IR (KBr): 2190 cm^{-1}. UV–vis (CH_2Cl_2): 402 (log ε 4.28), 751 (2.62), and 852 nm (2.91).

3.2.7. Bis(tributylphosphine)(dithiolenato)platinum(II) (5)

A solution of TTF(SnMe$_3$)$_2$ (**2b**) (0.31 g, 0.6 mmol) in CH_2Cl_2 (5 ml), prepared according to the procedure described in Section 3.2.3, was slowly added to a flask containing (COD)PtCl$_2$ (0.45 g, 1.2 mmol) at −90 °C under nitrogen. After warming to room temperature, the mixture was stirred overnight. Tributylphosphine (1.2 ml, 4.8 mmol) was added and furthermore stirred for 2 days. After evaporation, the residue was chromatographed on Al$_2$O$_3$ to give a yellow oil, which was dissolved in a small amount of diethyl ether and then chilled at −90 °C. The title complex was obtained as pale yellow crystals (44 mg, 11%). M.p. 100 °C. Anal. Found: C, 45.58; H, 8.20%. $C_{26}H_{56}P_2PtS_2$ calc.: C, 45.26; H, 8.18%. IR (KBr): 1093, 1463 (C=C), and 2998 cm^{-1} (CH). Raman: 1496 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.93 (t, 18H, Me), 1.40–1.56 (m, 24H, CH$_2$), 2.01–2.05 (m, 12H, CH$_2$), and 6.66 (d, $^4J_{P,H} = 4.1$ Hz, $^3J_{Pt,H} = 76.9$ Hz, 2H, CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.72 (Me), 24.16 (t, $^3J_{P,C} = 14.0$ Hz, γ-CH$_2$), 25.48 (m, α-CH$_2$), 26.20 (t, $^2J_{P,C} = 18.3$ Hz, β-CH$_2$), and 126.41 (t, $^3J_{P,C} = 14.8$ Hz, $^2J_{Pt,C} = 55.7$ Hz, =CH). ^{31}P NMR (162 MHz, CDCl$_3$): δ −3.47 ($^1J_{Pt,P} = 2729$ Hz).

3.2.8. Tetraiodotetrathiafulvalene (8) [23]

To the solution of LDA, prepared from n-BuLi (3.1 ml, 5 mmol) and (i-Pr)$_2$NH (0.7 ml, 5 mmol) in THF (10 ml) at −78 °C, was added a solution of TTF (0.10 g, 0.49 mmol) in THF (10 ml). After the solution had been stirred for 2.5 h at the temperature, I$_2$ (1.3 g, 5 mmol) was added to the solution at −78 °C. The solution was stirred for 1 h and then the solution was warmed slowly to room temperature. The solution was reduced by a small amount of aqueous ascorbic acid and sodium thiosulfate. The resulting crystals were filtrated and washed with CH_2Cl_2. Red crystals (90 mg, 26%). M.p. 196–202 °C (dec.). MS (EI): m/z 707 (M$^+$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 79.72 (C–I) and 116.734 (C=C).

The filtrate was extracted with CH_2Cl_2 and the extract was dried over MgSO$_4$. After evaporation, the residue was chromatographed on SiO$_2$. The crystals obtained were recrystallized from CS$_2$–pentane to give diiodotetrathiafulvalene (**9**) [23] as deep red crystals (24 mg, 11%). ^{1}H NMR (CDCl$_3$): δ 6.42 (s, C–H for

cis-isomer) and 6.43 (s, C–H for trans-isomer). ^{13}C NMR (CDCl$_3$): 63.46 (C–I), 123.97 (CH for trans-isomer), and 124.11 (CH for cis-isomer). The assignment of cis- or trans-isomers may be inverse.

4. Structure determination

The crystallographic data are summarized in Table 1 and the position parameters for complexes **3**, **2a**, and **5** are listed in Tables 4–6 respectively.

Oscillation and non-screen Weissenberg photographs

Table 4
Position parameters and U_{iso} for complex **3**

Atom	x/a	y/b	z/c	U_{iso}
Sn(1)	0.31447(3)	0.26342(4)	0.29140(3)	0.051
Sn(2)	0.25970(3)	−0.09589(4)	0.27198(3)	0.054
S(1)	0.44717(11)	0.15485(15)	0.43489(9)	0.051
S(2)	0.39828(12)	−0.08917(16)	0.42714(11)	0.061
C(1)	0.4684(4)	0.0127(6)	0.4723(3)	0.048
C(2)	0.3663(4)	0.1166(6)	0.3599(3)	0.047
C(3)	0.3437(4)	0.0038(6)	0.3558(3)	0.050
C(4)	0.3789(5)	0.4127(6)	0.3466(4)	0.062
C(5)	0.4459(6)	0.4426(8)	0.3331(6)	0.098
C(6)	0.4894(8)	0.5390(10)	0.3693(8)	0.132
C(7)	0.4642(8)	0.6023(9)	0.4181(8)	0.120
C(8)	0.3946(10)	0.5750(11)	0.4307(7)	0.142
C(9)	0.3488(7)	0.4777(8)	0.3941(6)	0.105
C(10)	0.3276(4)	0.2484(7)	0.1850(4)	0.062
C(11)	0.3573(6)	0.1466(10)	0.1654(5)	0.092
C(12)	0.3681(7)	0.1408(14)	0.0945(7)	0.128
C(13)	0.3478(9)	0.2356(19)	0.0468(7)	0.143
C(14)	0.3173(8)	0.3363(16)	0.0660(7)	0.138
C(15)	0.3060(7)	0.3448(10)	0.1366(5)	0.110(
C(16)	0.2007(4)	0.2796(6)	0.2928(4)	0.064
C(17)	0.1437(5)	0.3244(8)	0.2297(5)	0.075
C(18)	0.0703(6)	0.3424(9)	0.2333(6)	0.095
C(19)	0.0523(6)	0.3182(10)	0.2974(6)	0.099
C(20)	0.1098(6)	0.2751(10)	0.3592(6)	0.101
C(21)	0.1838(6)	0.2526(8)	0.3560(5)	0.081
C(22)	0.1684(5)	−0.0021(7)	0.1919(4)	0.059
C(23)	0.1750(5)	0.0280(8)	0.1233(5)	0.079
C(24)	0.1130(7)	0.0809(11)	0.0700(5)	0.100
C(25)	0.0450(7)	0.0993(10)	0.0861(6)	0.100
C(26)	0.0369(6)	0.0675(9)	0.1539(6)	0.093
C(27)	0.1007(5)	0.0171(8)	0.2068(5)	0.078
C(28)	0.2091(5)	−0.2072(7)	0.3338(4)	0.065
C(29)	0.1959(6)	−0.1673(9)	0.3957(5)	0.093
C(30)	0.1601(7)	−0.2374(11)	0.4362(7)	0.115
C(31)	0.1406(8)	0.3512(12)	0.4119(8)	0.137
C(32)	0.1538(9)	−0.3934(10)	0.3495(9)	0.156
C(33)	0.1883(7)	−0.3214(9)	0.3085(7)	0.127
C(34)	0.3240(5)	−0.1897(7)	0.2151(4)	0.074
C(35)	0.2859(7)	−0.2510(11)	0.1517(6)	0.115
C(36)	0.3267(10)	−0.3134(13)	0.1130(8)	0.152
C(37)	0.4060(10)	−0.3166(13)	0.1416(8)	0.144
C(38)	0.4442(8)	−0.2583(15)	0.2054(8)	0.152
C(39)	0.4033(7)	−0.1915(12)	0.2436(6)	0.113
C(40)	0.430(2)	0.007(5)	0.943(2)	0.238
C(41)	0.489(4)	0.094(3)	0.951(3)	0.284
C(42)	0.558(4)	0.083(3)	1.010(4)	0.319

were recorded on the imaging plates on a Mac Science DIP3000 diffractometer with graphite monochromated Mo Kα radiation and an 18 kW rotating anode generator. The data reduction and determination of cell parameters were made by the MAC DENZO program system. The structure was solved with the Dirdif–Patty method in CRYSTAN-GM (software-package for structure determination) and refined by full-matrix least squares procedure. Anisotropic refinements for non-hydrogen atoms

Table 5
Position parameters and U_{iso} for complex 2a

Atom	x/a	y/b	z/c	U_{iso}
Sn(1)	-0.87040	0.37000	-0.53310	0.056
Sn(2)	0.00280	0.00130	-0.00130	0.069
S(1)	-0.400(10)	0.381(7)	-0.332(4)	0.084
S(2)	-0.676(9)	0.198(6)	-0.361(3)	0.065
S(3)	-0.470(11)	-0.006(7)	-0.201(4)	0.086
S(4)	-0.239(10)	0.188(6)	-0.170(4)	0.083
C(1)	-0.46(3)	0.23(2)	-0.30(1)	0.078
C(2)	-0.55(3)	0.44(2)	-0.42(1)	0.098
C(3)	-0.68(4)	0.34(2)	-0.43(1)	0.073
C(4)	-0.40(3)	0.15(2)	-0.23(1)	0.057
C(5)	-0.31(3)	-0.04(2)	-0.12(1)	0.049
C(6)	-0.19(4)	0.03(2)	-0.10(1)	0.073
C(7)	-1.17(3)	0.56(2)	-0.52(1)	0.067
C(8)	-1.17(2)	0.62(2)	-0.45(1)	0.052
C(9)	-1.39(3)	0.76(2)	-0.14(1)	0.092
C(10)	-1.54(3)	0.79(2)	-0.50(1)	0.071
C(11)	-1.51(4)	0.72(2)	-0.56(1)	0.113
C(12)	-1.32(3)	0.59(2)	-0.57(1)	0.064
C(13)	-0.68(4)	0.42(2)	-0.63(1)	0.090
C(14)	-0.78(3)	0.55(2)	-0.68(1)	0.078
C(15)	-0.68(3)	0.60(2)	-0.74(1)	0.089
C(16)	-0.47(2)	0.47(1)	-0.78(1)	0.053
C(17)	-0.41(4)	0.36(2)	-0.73(1)	0.093
C(18)	-0.50(3)	0.32(2)	-0.66(1)	0.058
C(19)	-0.96(3)	0.17(2)	-0.56(1)	0.070
C(20)	-0.92(4)	0.12(2)	-0.63(1)	0.068
C(21)	-1.00(4)	0.00(2)	-0.63(2)	0.117
C(22)	-1.11(3)	0.05(2)	-0.57(1)	0.069
C(23)	-1.17(3)	0.01(2)	-0.52(1)	0.105
C(24)	-1.06(4)	0.12(2)	-0.50(1)	0.097
C(25)	0.11(3)	0.18(2)	0.02(1)	0.073
C(26)	0.21(3)	0.24(2)	-0.04(1)	0.075
C(27)	0.26(2)	0.35(1)	-0.03(1)	0.069
C(28)	0.23(3)	0.41(2)	0.06(1)	0.085
C(29)	0.10(3)	0.37(2)	0.11(1)	0.079
C(30)	0.04(4)	0.26(2)	0.10(1)	0.097
C(31)	-0.18(3)	-0.04(2)	0.10(1)	0.071
C(32)	-0.36(4)	0.07(2)	0.12(1)	0.115
C(33)	-0.48(4)	0.05(2)	0.19(1)	0.116
C(34)	-0.43(4)	-0.13(2)	0.22(1)	0.121
C(35)	-0.24(3)	-0.19(2)	0.21(1)	0.092
C(36)	-0.13(3)	-0.19(2)	0.14(1)	0.103
C(37)	0.29(3)	-0.19(2)	-0.03(1)	0.066
C(38)	0.31(3)	-0.24(2)	-0.11(1)	0.071
C(39)	0.48(3)	-0.35(2)	-0.12(1)	0.061
C(40)	0.63(2)	-0.43(1)	-0.06(1)	0.052
C(41)	0.62(3)	-0.35(2)	0.01(1)	0.072
C(42)	0.43(2)	-0.24(2)	0.03(1)	0.062

Table 6
Position parameters and U_{iso} for complex 5

Atom	x/a	y/b	z/c	U_{iso}
Pt(1)	0.95332(6)	0.19823(3)	0.30004(2)	0.067
S(1)	1.0508(5)	0.3042(3)	0.3545(2)	0.097
S(2)	1.1607t4)	0.1937(3)	0.2440(2)	0.101
P(1)	0.7635(4)	0.2138(2)	0.3641(2)	0.073
P(2)	0.8737(5)	0.0911(3)	0.2437(2)	0.086
C(1)	1.2120(17)	0.3183(9)	0.3240(8)	0.091
C(2)	1.2564(18)	0.2739(10)	0.2786(9)	0.108
C(3)	0.7002(17)	0.3187(10)	0.3674(8)	0.093
C(4)	0.6665(18)	0.3499(9)	0.3020(10)	0.101
C(5)	0.622(2)	0.438(1)	0.301(1)	0.133
C(6)	0.583(4)	0.464(2)	0.233(2)	0.231
C(7)	0.8145(16)	0.1964(11)	0.4438(6)	0.083
C(8)	0.839(2)	0.110(1)	0.456(1)	0.104
C(9)	0.885(3)	0.093(2)	0.523(1)	0.159
C(10)	0.909(3)	0.004(2)	0.535(1)	0.194
C(11)	0.6000(15)	0.1583(9)	0.3539(6)	0.080
C(12)	0.4837(19)	0.1693(9)	0.4035(8)	0.092
C(13)	0.368(2)	0.110(1)	0.398(1)	0.108
C(14)	0.256(2)	0.116(2)	0.447(1)	0.152
C(15)	0.6973(17)	0.1014(13)	0.2051(8)	0.108
C(16)	0.670(2)	0.184(2)	0.174(1)	0.127
C(17)	0.520(2)	0.180(2)	0.146(1)	0.144
C(18)	0.481(4)	0.262(2)	0.113(2)	0.238
C(19)	0.850(2)	-0.001(1)	0.287(1)	0.105
C(20)	0.982(2)	-0.036(1)	0.316(1)	0.121
C(21)	0.946(4)	-0.109(1)	0.359(1)	0.170
C(22)	1.079(5)	-0.144(2)	0.388(2)	0.237
C(23)	0.987(2)	0.057(2)	0.178(1)	0.151
C(24)	0.993(3)	0.101(2)	0.122(1)	0.172
C(25)	1.078(6)	0.054(4)	0.072(2)	0.289
C(26)	1.109(6)	0.106(3)	0.023(2)	0.318

were carried out. All the hydrogen atoms, partially located from a differential Fourier map, for complex 5 were isotropically refined. In complexes 2a and 3, no hydrogen was located.

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