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LETTERS

Synthesis and Properties of Bitetraselenafulvalene

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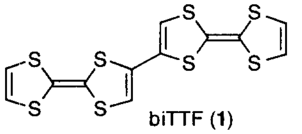
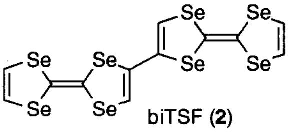
Abstract: Copper(II)- and palladium(II)-catalyzed homo-coupling reactions of trimethylstannyltetraselenafulvalene proceed smoothly to produce bitetraselenafulvalene (biTSF) in good yield. The X-ray analysis of biTSF shows an interesting crystal structure. The CT-complex and radical cation salts derived from biTSF indicate fairly high electric conductivities. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: coupling reactions; electron donors; physical properties; X-ray crystal structures.

Tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) have attracted much interest because of their electron-donating ability which has been used for the synthesis of new organic metals and superconductors.[1] In particular, extended π-donors based on the TTF framework have been investigated in recent years.[2] However, few extended TSF-based donors were known until now, although the charge transfer salts of TSF usually show better conductivities than those of TTF.[3] Recently, we reported an efficient synthesis of bitetrathiafulvalene (biTTF) **1** using the palladium-catalyzed homo-coupling reaction of trialkylstannyl-TTF.[4] We now report here a novel transition-metal-catalyzed synthesis, X-ray analysis and donor-properties of bitetraselenafulvalene (biTSF) **2**.

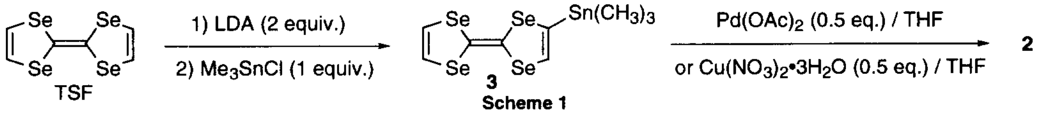


biTTF (**1**)



biTSF (**2**)

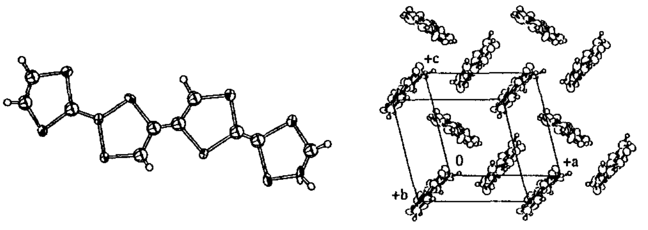
The synthesis of biTSF was carried out using the transition-metal-mediated coupling reaction (Scheme 1). Thus, TSF was first converted into the trimethylstannyl derivative (**3**), by treatment with LDA [2 equiv., THF, -78 °C], followed by the reaction with Me_3SnCl [1.1 equiv., -78 °C for 1 h, room temp. for 2 h]. The reaction of **3** with $Pd(OAc)_2$ (0.5 equiv.) in benzene at room temp. for 4 h led to biTSF **2** (33% overall yield from TSF), together with the recovered TSF (47%).[5] In a similar manner, the reaction of **3** with $Cu(NO_3)_2{\bullet}3H_2O$ in THF at room temp. for 2 h produced **2** in 39% overall yield, together with TSF (56%). Therefore, **2** can be synthesized totally in 87% yield based on the consumed TSF.



Scheme 1

PII: S0040-4039(99)01085-0

The structure of **2** was determined unambiguously by X-ray analysis (Figure 1).[6] Interestingly, the crystal lattice includes three crystallographically independent molecules. Figure 1a shows the molecular structure of one of the zig-zag molecules, Figure 1b indicating the packing mode of **2** along with the b-axis. Two of the crystallographically independent molecules, which dimerize, are found to have essentially the same zig-zag conformation, whereas the third one has an almost planar structure. There are numerous Se•••Se short contacts which lead to the formation of the unique packing structure of **2**.



(a) (b)

Figure 1. ORTEP Drawings of **2**. (a) Top View of the molecular structure. (b) The packing diagram.

Table 1. Redox potentials.[a)]

Compound	$E^1_{1/2}$	$E^2_{1/2}$
TTF	0.36	0.73
TSF	0.49	0.82
biTTF **1**	0.43	0.84
biTSF **2**	0.45	0.71[b)]

[a)] Conditions: n-Bu_4NClO_4 (0.1 mol dm^{-3}), benzonitrile, 20 °C, vs. SCE (Ag/Ag$^+$ reference electrode). [b)] The anodic potential.

The oxidation potentials of TTF, TSF, **1**, and **2** measured by cyclic voltammetry are shown in Table 1.[7] Although the solubility of **2** is fairly low in common organic solvents, well-assignable voltammograms were obtained in benzonitrile as the solvent. In a similar manner as **1**, biTSF **2** shows only two redox waves, in which the first process seems to be a two-electron oxidation to form the dication-diradical species. The second redox process in **2** was irreversible, reflecting the instability of the tetracationic species. In spite of the instability of the cationic species in **2**, the first oxidation potential of **2** is lower than that ($E^1_{1/2}$ = 0.55 V) of BEDT-TTF. Therefore, biTSF **2** can be expected to show good donor ability.

Since **2** can be expected to show highly conducting CT and radical ion salts due to the effect of stoichiometric control,[8] we investigated the CT-complex and radical ion salts of **2**. The donor **2** formed the CT complex with TCNQ, and the electrocrystallization of **2** gave the corresponding radical ion salts as very fine microcrystals. All electrical conductivities were measured using compressed pellets (Table 2). The radical ion salts [$2{\bullet}ClO_4^-$, $(2)_3{\bullet}(PF_6)_2$, $(2)_3{\bullet}(I_3)_2$, and $(2)_2.FeCl_4$] indicate fairly high conductivities except for $2{\bullet}$TCNQ and $(2)_3{\bullet}(BF_4)$. The conductivities of these salts are higher than those derived from **1**.[8] Work on the X-ray structure measurement of single-crystals of the radical ion salts is now in progress.

Table 2. Electrical conductivities of CT-complexes and radical ion salts derived from **2**.

Acceptor	Solvent	D:A[a]	σ_{rt}[b]/S cm^{-1}
TCNQ	PhCN	1:1	5.6×10^{-2}
ClO_4^-	CS_2-PhCl	1:1	1.2
PF_6^-	CS_2-PhCl	3:2	4.2
I_3^-	CS_2-DCE[c]	3:2	2.5
BF_4^-	CS_2-PhCl	3:1	0.16
$FeCl_4^-$	CS_2-PhCl	2:1	1.2

[a)] Determined by elemental analysis. [b)] Room-temperature conductivity measured on a compresed pellet by a four-probe technique. [c)] 1,2-Dichloroethane.

References and Notes

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5. Selected physical data of **2**: reddish orange needles, FAB-MS (positive, *m*-nitrobenzyl alcohol) *m/z* 781, 783, 785, 787 (M+1); ^{1}H NMR (CS_2-CD_2Cl_2 10:1) δ 6.889 (s, 2H), 7.220 (d, J = 7.0 Hz, 2H), 7.231 (d, J = 7.0 Hz, 2H).
6. Crystal data for **2**: $C_{12}H_6Se_8$, Mw = 781.86, triclinic, space group *P1* (#1), a = 10.249(1), b = 15.559(2), c = 8.759(1) Å, α = 100.46(1)°, β = 105.07(1)°, γ = 72.550(9)°, V = 1278.5(3) Å^3, Z = 3, Dc = 3.046 g cm^{-3}, R = 0.031, Rw = 0.030 for 2760 observed reflections out of 5887 unique reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
7. Potentials were measured against an Ag/Ag$^+$ reference electrode and converted to the value *vs.* SCE (Fe/Fe$^+$ = +0.31 V).
8. For the conductivities of radical salts of biTTF derivatives, see, Iyoda, M.; Ogura, E.; Hara, K.; Kuwatani, Y.; Nishikawa, H.; Sato, T.; Kikuchi, K.; Ikemoto, I.; Mori, T. *J. Mater. Chem.*, **1999**, *9*, 335.