

New potential (P,S)-ligands containing tetrathiafulvalene

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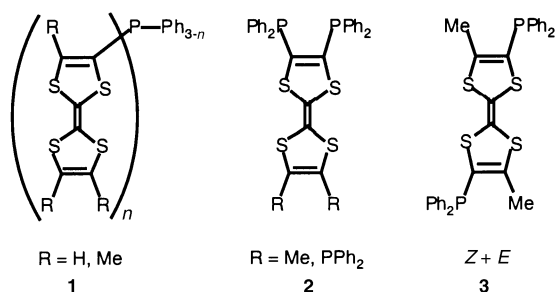
The synthesis of novel (P,S)-ligands containing tetrathiafulvalene (TTF) from preformed TTF derivatives is reported. These compounds were prepared by using borane as protecting group for the phosphine. The electrochemical properties of these new ligands are presented.

Among the various functionalized tetrathiafulvalenes (TTFs) described in the literature¹ only a few examples of these organic donors are substituted with coordination functions.²⁻⁶ From the viewpoint of molecular materials, phosphine substituents, thanks to their chelating ability towards low- and high-oxidation-state transition metal derivatives, offer the possibility of forming organic-inorganic hybrid building blocks.^{6,7} Association of the TTFs, well known for their redox properties, with one or more appropriate metals will lead to a hybrid molecule with multiple redox sites. Various potential applications can be considered for these hybrid molecules such as in molecular materials or in catalytic activity.^{2,7} The TTF-functionalized phosphine ligands described so far involved one or more diphenylphosphino substituents directly linked to the donor core (1-3).²⁻⁶ Our goal was to introduce a spacer between the

phosphine-borane substituents was realized starting either from dibromo-TTF **4** or bis(cyanoethylthio)-TTF **5** as outlined in Scheme 1.^{13,†} It is worth noting that **4** is less stable and more difficult to purify than **5**. Nevertheless, addition of the lithium salt of diphenylphosphine-borane, $\text{Ph}_2\text{P}(\text{Li})\text{BH}_3$, to **4** at low temperature afforded bisphosphine-borane TTF **6**. Bis(cyanoethylthio)-TTF **5** was used as the precursor in our second approach for the synthesis of compound **6**. Becher and co-workers have recently demonstrated that the use of cyanoethyl-protected TTF-thiolate is an efficient building block for the preparation of a wide range of TTF derivatives as well as dendritic compounds or cyclophanes containing one or two TTF units.¹⁴ The advantage of bis(cyanoethylthio)-TTF **5** is not only connected with its stability when compared with **4** but also to the fact that deprotection of one thiolate group can be selectively achieved.¹⁴ Depending on the amount of the base used either the mono- or the bis-thiolate TTF was generated in the medium, and can further react with various electrophiles. In order to prepare bisphosphine-borane-TTF we chose 3-iodopropyl(diphenyl)phosphine which was prepared by action of $\text{Ph}_2\text{P}(\text{Li})\text{BH}_3$ on 1,3-diiodopropane in tetrahydrofuran (THF) at -80°C under argon (Scheme 1).

Bis(cyanoethylthio)-TTF **5** in the presence of two equivalents of caesium hydroxide yielded the dithiolate; reaction of this intermediate with iodopropyl(diphenyl)phosphine-borane afforded the TTF **6** in good yield. As it has been pointed out by Becher, deprotection of one thiolate can be performed with one equivalent of caesium hydroxide. Actually, we used that possibility in order to prepare the mono(phosphino-borane)-substituted TTF **8** (Scheme 2). After the addition of base, the thiolate generated *in situ* reacted with iodomethane and the TTF **7** was obtained. Then treatment of this TTF with another equivalent of caesium hydroxide, followed by the addition of iodopropyl(diphenyl)phosphine-borane, led to the TTF **8**.

Phosphine-borane-TTFs **6** and **8**, due to their stability, can be stored as precursors for further work. Decomplexation of phosphine-borane complexes in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) under inert atmosphere gave the phosphine derivatives **9** and **10** in good yields (Scheme 3).¹² These phosphine ligands are moderately air stable in solution. Both phosphine TTF **9** and **10** exhibit similar phosphorus chemical shifts (δ_{p} -16.4 ppm). This chemical shift is close

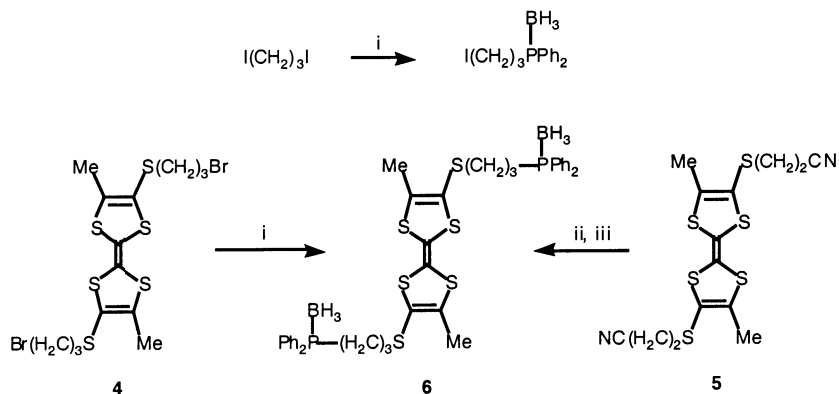


phosphorus atom and the TTF and to form a potentially bidentate ligand by adding a sulfide function. Indeed, ambidentate ligands such as (P,S) ones, due to the different lability of the phosphorus-metal and sulfur-metal bond, have been recently investigated in catalytic asymmetric reactions.⁸⁻¹⁰ In this paper, we describe the synthesis of new ligands containing the redox-active TTF moiety together with their electrochemical properties.

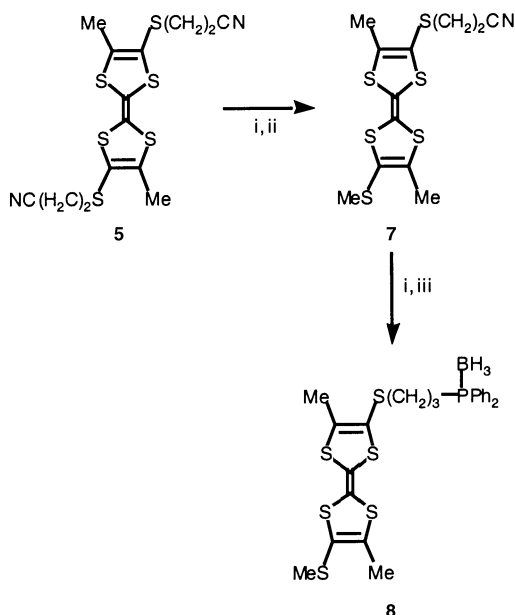
Results and discussion

In order to build these new ligands we used preformed TTF derivatives and then we functionalized these donors with the appropriate substituents. The use of phosphine-borane complexes in the synthesis of phosphino-TTF presents several advantages. On one hand, these complexes are very stable compared with phosphine derivatives, not sensitive towards the usual oxidizing or electrophilic reagents¹⁰ and very easy to use in organic synthesis.¹¹ On the other hand, decomplexation of phosphine-borane is simply realized using a soft method which does not interact with the TTF core.¹² The grafting of

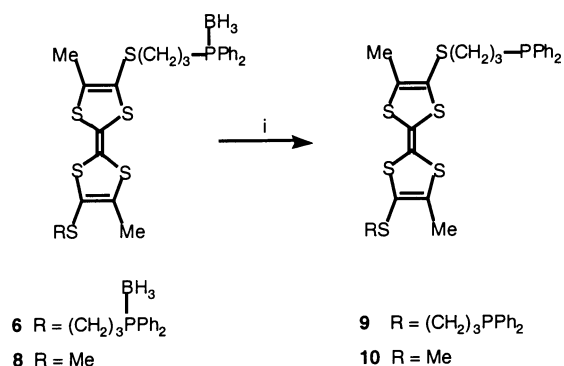
† As details of compound **5** have not yet been published, its data are reported below: yield 70%; mp 174°C ; R_f (SiO_2 ; CH_2Cl_2) 0.56; δ_{H} (200 MHz; CDCl_3) 2.18 (s, 6H), 2.65 (t, 4H), 2.95 (t, 4H); δ_{C} (75 MHz; CDCl_3) 16.23, 19.12, 31.47, 109.40, 116.90, 118.27, 139.12; MS (EI) 401.949 (M^+) (Found: C, 41.84; H, 3.44; N, 6.54; S, 47.56. $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_6$ requires C, 41.75; H, 3.50; N, 6.95; S, 47.80%).



Scheme 1 Reagents and conditions: i, $\text{Ph}_2\text{P(Li)BH}_3$, THF, -80°C ; ii, $\text{CsOH}\cdot\text{H}_2\text{O}$ (2.1 equiv.); iii, $\text{I(CH}_2\text{)}_3\text{PBH}_2\text{Ph}_2$.



Scheme 2 Reagents and conditions: i, $\text{CsOH}\cdot\text{H}_2\text{O}$ (1 equiv.); ii, MeI; iii, $\text{I(CH}_2\text{)}_3\text{PBH}_2\text{Ph}_2$.



Scheme 3 Reagents and conditions: i, DABCO.

to that observed for P,S ligands such as 2,5-bis[2-(diphenylphosphino)ethyl]thiophene ($\delta_{\text{P}} -16.6$ ppm).⁹

The donor abilities of these TTFs were studied by cyclic voltammetry (CV). It is worth noting that the presence of the phosphine-borane on the side-chain slightly increases the donor ability of the TTF core. This could be explained by a possible complexation of the exocyclic sulfurs with the borane which would deactivate the withdrawing effect of the sulfur. The more anodic oxidation potentials for the dimethylbis-(methylthio)-TTF (DMBMT-TTF) are in favour with this hypothesis. CV data for TTFs **6**, **8**–**10** and DMBMT-TTF are collated in Table 1.

Table 1 CV data, E in V vs. SCE, Pt working electrode with 0.1 M $n\text{-Bu}_4\text{NPF}_6$, scanning rate 100 mV s^{-1} in CH_2Cl_2

Compound	E_{pa}^1	E_{pa}^2	ΔE (mV)
DMBMT-TTF	0.43	0.81	380
6	0.39	0.83	440
8	0.40	0.84	440
9	0.49	0.86 ^a	370
10	0.44	0.84 ^a	400

^a Quasi-irreversible process.

Our synthetic approach allowed us to prepare P,S hybrid ligands containing TTF with a propyl chain between the sulfur atom and the phosphorus one. The scope of this synthesis can now be broadened to related P,S ligands by the introduction of a cyclic or aliphatic bridging chain of variable length. The next step of this work will be to study the ability of these ligands to coordinate different metals. Application of these ligands can be easily foreseen for molecular materials and/or catalytic activities. Within this framework, and depending on the metal centre coordinated, we can tune the redox properties of the TTF. This can be achieved by substituting these donors by either electron-donating or -withdrawing groups instead of the methyl one.

Experimental

Mps were measured on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses were performed at the Laboratoire Central de Microanalyse du CNRS, Lyon. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker ARX 200 or Bruker AC 300P spectrometers. Chemical shifts are quoted in parts per million (ppm) referenced to tetramethylsilane for ^1H NMR and ^{13}C NMR and to H_3PO_4 for ^{31}P NMR. Coupling constants (J) are reported in Hertz. Mass spectra were recorded with a Varian MAT 311 instrument by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. THF was distilled from sodium-benzophenone. Methanol was dried over calcium. Toluene was dried over sodium wire. Chromatography was performed using silica gel Merck 60 (70–260 mesh). CV was carried out on a 10^{-3} M solution of TTF derivatives in dichloromethane, containing 1.0 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte. Voltammograms were recorded at 0.1 V s^{-1} at a platinum disk electrode ($A = 1\text{ mm}^2$). The potentials were measured versus Saturated Calomel Electrode (SCE). As previously observed with bis-functionalized TTFs, all the TTFs synthesized and described below are present as two isomers (Z/E) which were observed by ^1H and ^{13}C NMR spectroscopy but not separated (only the E isomers are presented in the Schemes).¹⁵ Light petroleum (LP) refers to the fraction with distillation range $40\text{--}60^\circ\text{C}$.

Iodopropyl(diphenyl)phosphine–borane

A mixture of $\text{PPh}_3 \cdot \text{BH}_3$ (2.76 g, 10 mmol), lithium divided in small pieces (140 mg, 20 mmol) and 20 mL of freshly distilled THF was vigorously stirred under argon for 5 h. After cooling of the mixture at 0 °C in an ice-bath, $t\text{BuCl}$ (1.1 mL, 10 mmol) was added slowly. The solution was stirred for another hour at RT. This solution was added to a solution of 1,3-diiodopropane (1.19 mL, 10 mmol) in 20 mL of dried THF at –80 °C and the mixture was allowed to warm to RT over a period of 12 h. Acidic hydrolysis with 1 M HCl, extraction with CH_2Cl_2 , and purification by chromatography over silica gel (2:1 CH_2Cl_2 –LP) afforded 3-iodopropyl(diphenyl)phosphine–borane (0.48 g, 30%) as a white powder, mp < 40 °C; R_f 0.68; δ_{H} (200 MHz; CDCl_3) 0.60–1.30 (m, 3H), 2.00 (m, 2H), 2.34 (m, 2H), 3.22 (t, 2H, J 6.8), 7.26–7.74 (m, 10H); δ_{P} (121 MHz; CDCl_3) 15.55; δ_{C} (50 MHz; CDCl_3) 8.07, 27.51, 27.56, 129.59, 129.60, 132.04, 132.76 (Found: $[\text{M} - \text{H}]^+$, 367.0281. $\text{C}_{15}\text{H}_{18}\text{BP}$ requires m/z , 367.0287).

3,3'-Bis[3-(boranatodiphenylphosphino)propylthio]-4,4'-dimethyltetrafulvalene 6

From the bisbromo-TTF 4. A mixture of $\text{PPh}_3 \cdot \text{BH}_3$ (276 mg, 1 mmol), lithium divided in small pieces (14 mg, 2 mmol) and 2 mL of freshly distilled THF was vigorously stirred under argon for 5 h at RT. After cooling of the mixture at 0 °C in an ice-bath, $t\text{BuCl}$ (110 μL , 1 mmol) was slowly added. The solution was stirred for another hour at RT, then was added to a solution of the dibromo-TTF **4**¹³ (269 mg, 0.5 mmol) in 5 mL of dried THF at –80 °C. The mixture was allowed to reach RT and was stirred overnight. Acidic hydrolysis, extraction with CH_2Cl_2 , rotary evaporation, and purification over silica gel (2:1 CH_2Cl_2 –LP) afforded *title fulvalene 6* (0.16 g, 21%) as a yellow powder.

From the bis(cyanoethylthio)-TTF 5. To a solution of the bis(cyanoethylthio)-TTF **5** (402 mg, 1 mmol) in 20 mL of DMF was added under argon a solution of $\text{CsOH} \cdot \text{H}_2\text{O}$ (353 mg, 2.1 mmol) in 5 mL of MeOH. The mixture was stirred for 30 min at RT, after which 3-iodopropyl(diphenyl)phosphine–borane (736 mg, 2 mmol) was added. Stirring was continued for 1 h. Solvents were removed by rotary evaporation, and the residue was extracted with CH_2Cl_2 and washed with water. Chromatography over silica gel (2:1 CH_2Cl_2 –LP) afforded *title fulvalene 6* (0.48 g, 62%) as a yellow powder, mp 183–184 °C; R_f 0.53; δ_{H} (200 MHz; CDCl_3) 0.67–1.25 (m, 6H), 1.72–1.91 (m, 4H), 2.05 (s, 6H), 2.25–2.39 (m, 4H), 2.76 (t, 4H), 7.43–7.70 (m, 20H); δ_{P} (121 MHz; CDCl_3) 16.68; δ_{C} (75 MHz; CDCl_3) 15.87, 23.76, 24.93, 37.37, 108.0, 118.3, 129.34, 129.49, 131.75, 132.54, 136.22 (Found: M^{++} , 776.1442. $\text{C}_{38}\text{H}_{44}\text{B}_2\text{P}_2\text{S}_6$ requires M , 776.1442. Found: C, 58.49; H, 5.70. B, 2.81; P, 7.40. $\text{C}_{38}\text{H}_{44}\text{B}_2\text{P}_2\text{S}_6$ requires C, 58.76; H, 5.71; B, 2.78; P, 7.97%).

3-(2-Cyanoethylthio)-4,4'-dimethyl-3'-(methylthio)tetrathiafulvalene 7

To a solution of the bis(cyanoethylthio)-TTF **5** (1.0 g, 2.49 mmol) in 30 mL of DMF was added, under argon, a solution of $\text{CsOH} \cdot \text{H}_2\text{O}$ (0.42 g, 2.49 mmol) in 5 mL of MeOH. The mixture was stirred for 15 min at RT, after which CH_3I (0.2 mL, 3.2 mmol) was added. Stirring was continued for 30 min. Solvents were removed by rotary evaporation, and the residue was extracted with CH_2Cl_2 and washed with water. Chromatography over silica gel (2:1 CH_2Cl_2 –LP) afforded *title compound 7* (0.6 g, 66%) as an orange powder, mp 101–102 °C; R_f 0.45; δ_{H} (200 MHz; CDCl_3) 2.19 (s, 3H), 2.25 (s, 3H), 2.38 (s, 3H), 2.71 (t, 2H), 3.00 (t, 2H); δ_{C} (75 MHz; CDCl_3) 15.25, 15.64, 18.48, 19.42, 30.86, 107.26, 110.44, 116.20, 117.73, 120.86, 133.70, 138.55 (Found: C, 39.71; H, 3.45; N, 3.93; S, 52.84. $\text{C}_{12}\text{H}_{13}\text{NS}_6$ requires C, 39.64; H, 3.60; N, 3.85; S, 52.91%).

3-[3-(Boranatodiphenylphosphino)propylthio]-4,4'-dimethyl-3'-(methylthio)tetrathiafulvalene 8

To a solution of the TTF **7** (363 mg, 1 mmol) in 20 mL of DMF was added, under argon, a solution of $\text{CsOH} \cdot \text{H}_2\text{O}$ (0.2 g, 1.2 mmol) in 5 mL of MeOH. The mixture was stirred for 30 min at RT after which 3-iodopropyl(diphenyl)phosphine–borane (368 mg, 1 mmol) was added. Stirring was continued for 1 h. Solvents were removed by rotary evaporation, and the residue was extracted with CH_2Cl_2 and washed with water. Chromatography over silica gel (2:1 CH_2Cl_2 –LP) afforded *title fulvalene 8* (0.5 g, 91%) as an orange powder, mp 99–100 °C; R_f 0.61; δ_{H} (200 MHz; CDCl_3) 0.60–1.40 (3H), 2.02 (m, 2H), 2.22 (s, 3H), 2.31 (s, 3H), 2.48 (m, 2H), 2.49 (s, 3H), 2.94 (t, 2H), 7.65–7.89 (m, 10H); δ_{C} (50 MHz; CDCl_3) 15.65, 15.90, 19.79, 23.78, 24.88, 37.28, 108 (br, 2C), 118.6, 121.6, 129.35, 129.47, 131.78, 132.52, 134.10, 136.16; δ_{P} (121 MHz; CDCl_3) 16.33 (Found: M^{++} , 550.0337. $\text{C}_{24}\text{H}_{28}\text{BPS}_6$ requires M , 550.0351. Found: C, 52.27; H, 4.95; P, 5.67; S, 34.17. $\text{C}_{24}\text{H}_{28}\text{BPS}_6$ requires C, 52.35; H, 5.12; P, 5.62; S, 34.93%).

3,3'-Bis[3-(diphenylphosphino)propylthio]-4,4'-dimethyltetrafulvalene 9

To a solution of the TTF **6** (201 mg, 0.5 mmol) in 20 mL of dried, degassed toluene was added, under argon, DABCO (112 mg, 1 mmol). The mixture was stirred for 3–4 h at 50 °C. The reaction was followed by TLC. Toluene was evaporated off with a vacuum pump, and the residue was chromatographed under inert atmosphere with degassed solvents to afford the TTF **9** as an orange oil (224 mg, 60%), R_f (SiO_2 ; 2:1 CH_2Cl_2 –LP) 0.62; δ_{H} (200 MHz; CDCl_3) 1.62–1.80 (m, 4H), 2.04 (s, 6H), 2.13 (m, 4H), 2.80 (t, 4H), 7.30–7.75 (m, 20H); δ_{C} (50 MHz; CDCl_3) 15.42, 26.17, 26.92, 37.10, 108.33, 119.08, 128.53, 128.55, 130.88, 132.72, 135.14; δ_{P} (121 MHz; CDCl_3) –16.47 (Found: $[\text{M} + \text{H}]^+$, 749.0851. $\text{C}_{38}\text{H}_{39}\text{P}_2\text{S}_6$ requires m/z , 749.0854).

3-[3-Diphenylphosphino)propylthio]-4,4'-dimethyl-3'-(methylthio)tetrathiafulvalene 10

Same procedure as for **9**, applied to **8**. The TTF **10** was obtained as an orange oil (235 mg, 88%), R_f (SiO_2 ; 2:1 CH_2Cl_2 –LP) 0.75; δ_{H} (300 MHz; CDCl_3) 1.72 (m, 2H), 2.04 (s, 3H), 2.12 (s, 3H), 2.13 (m, 2H), 2.31 (s, 3H), 2.80 (t, 2H), 7.22–7.36 (m, 10H); δ_{C} (50 MHz; CDCl_3) 15.61, 15.80, 19.76, 26.60, 27.34, 37.51, 108.50, 109.00, 119.52, 121.25, 128.97, 129.05, 133.12, 134.06, 135.49, 138.72; δ_{P} (121 MHz; CDCl_3) –16.43 (Found: M^{++} , 536.0019. $\text{C}_{24}\text{H}_{25}\text{PS}_6$ requires M , 536.0018).

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