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# Ruthenium complexes of furan- and thiophene-thiolates: Structure of CpRu(dppe)SThi

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## Abstract

Complexes of ruthenium containing 2-furan- and 2-thiophene-thiolates with phosphine ligands have been prepared and characterized. The bis(triphenylphosphine) complexes  $CpRu(PPh_3)_2SR$  ( $R = C_4H_3O$ : Fu (1a),  $C_4H_3S$ : Thi (1b)) were prepared by the reaction of thiolato anions (FuS<sup>-</sup> or ThiS<sup>-</sup>) with  $CpRu(PPh_3)_2Cl$ . The one-pot reaction of  $CpRu(PPh_3)_2Cl$ , thiolato anions and L ligands gave CpRu(L)SR (L = bis(diphenylphosphino)methane: dppm (2); bis(diphenylphosphino)ethane: dppe (3)). The newly prepared complexes have been characterized by spectroscopic techniques (FT-IR, <sup>1</sup>H NMR and <sup>31</sup>P NMR) and by elemental analysis. The crystal structure of CpRu(dppe)SThi (3b) has been determined by X-ray diffraction.

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# 1. Introduction

The interest in complexes which incorporate thiolato ligands is stimulated by several important reasons [1–6]. These include the relevance to biological systems [7–13], industrial applications [14–16], the quest for novel structures of thiolato complexes and their applications in organosulfur chemistry [17,18].

The ruthenium thiolato complexes  $CpRu(PPh_3)_2SR$  are well documented. They have been synthesized by simple substitution reactions of  $CpRu(PPh_3)_2Cl$  with thiolato anions [19–25]. These complexes are found to be reactive due to the presence of two bulky triphenylphosphine ligands, which have a 145° cone angle [19]. Reactions of these complexes with CO or NO<sup>+</sup> at room temperature

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produced the carbonyl-substituted complexes  $CpRu(PPh_3)(CO)SR$  or the nitrosyl salts  $[CpRu(PPh_3)(-NO)SR]^+$ , respectively [19,21,26]. Protonation and alkylation of these thiolates occurred at the sulfur center with the generation of thiols or thioether complex salts [19,27].

The chemistry of ruthenium complexes containing heterocyclic thiolates has been studied in our laboratory [22,28]. The interaction of 2-pyridine thiolate and 2-pyrimidine thiolate with CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl gave the complexes  $CpRu(PPh_3)(\kappa^2 S, N-SR)$  (R = C<sub>5</sub>H<sub>4</sub>N, C<sub>5</sub>H<sub>3</sub>N<sub>2</sub>) in which the heterocyclic thiolato ligand is bonded to Ru in a chelating manner through both S and N atoms. Treatment of the latter complexes with CO at room temperature gave the mixed carbonyl-phosphine complexes  $CpRu(PPh_3)$ (CO)( $\kappa$ S-SR) [28]. The analogous reactions with NO-salt gave, unexpectedly the nitrosyl complexes  $[CpRu(PPh_3)]$  $(NO)(\kappa S-HSR)]^{2+}$ , which contain coordinated thiol ligands. The dppe-complexes  $CpRu(dppe)(\kappa S-SR)$  (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) were prepared by the reaction of

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CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl, thiolato anions and dppe ligand [28]. However, the reactions of CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl with the 2-mercaptobenzimidazolyl, 2-mercaptobenzoxazolyl and 2-mercaptobenzthiazolyl thiolates gave the expected thiolato complexes CpRu(PPh<sub>3</sub>)<sub>2</sub>( $\kappa$ S-SR) in which the thiolato ligand is bonded in a monodentate fashion through the S-atom of these thiolates [22]. In a similar way to that described for 2-pyridine- and 2-pyrimidine thiolates, the complexes CpRu(PPh<sub>3</sub>)(CO)( $\kappa$ S-SR) and CpRu(L)( $\kappa$ S-SR) (SR = 2-mercaptobenzimidazolyl, 2-mercaptobenzoxazolyl, 2-mercaptobenzthiazolyl, L = dppe, dppm) were obtained [22].

Extending our work on the synthesis of heterocyclic thiolato complexes of ruthenium [22,28] and searching for mono- versus bi-dentate coordination of heterocyclic ligands, we report in this paper the synthesis and character-ization of ruthenium complexes containing 2-furan- and 2-thiophene thiolato complexes. We show that the thiolates employed act as terminal ligands in these complexes.

# 2. Results and discussion

# 2.1. Synthesis and characterization

Ruthenium complexes of the formulae  $CpRu(PPh_3)_2$ SFu and  $CpRu(PPh_3)_2$ SThi (Fu = C<sub>4</sub>H<sub>3</sub>O (1a), Thi = C<sub>4</sub>H<sub>3</sub>S (1b)) are readily prepared by the reaction of CpRu(PPh\_3)\_2Cl with the thiolato anions (FuS<sup>-</sup>, ThiS<sup>-</sup>) in refluxing THF for a short time (Scheme 1). The thiolato anions were generated by the lithiation of the five membered heterocyclic compound using MeLi followed by the addition of elemental sulfur. These ligands were used as solutions and were not isolated as solids.

The yellow complexes 1 are air stable as solids but highly sensitive to air in solution. They are soluble in most common organic solvents and are insoluble in hexane. The



 $E = O(a), S(b), P-P= Ph_2PCH_2PPh_2 (dppm) 2, Ph_2PCH_2CH_2PPh_2 (dppe) 3$ 

compounds have been characterized by <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy as well as by elemental analysis. The main NMR-spectroscopic features of 1 are a singlet in the  $^{1}$ H NMR spectrum, in the range of 4.15–4.17 ppm for the Cp-ring protons and a singlet in the <sup>31</sup>P NMR spectrum. in the range of 44.54–44.55 ppm for the equivalent P atoms of the triphenylphosphine ligands. These Cp protons for 1 are within the same range of chemical shifts observed for similar thiolato complexes  $CpRu(PPh_3)_2SR$  (R = alkyl, arvl, pyridine, pyrimidine: 4.12–4.38 ppm) [19,21,28] and are lower than those observed for  $CpRu(PPh_3)_2SR$ (SR = 2-mercaptobenzimidazolyl, 2-mercaptobenzoxazolvl, 2-mercaptobenzthiazolvl: 4.76–4.85 ppm) [22]. The <sup>31</sup>P NMR signal of 1 is slightly lowfield shifted compared to those of  $CpRu(PPh_3)_2SR$  (SR = 2-mercaptobenzimidazol-2-mercaptobenzoxazolyl, 2-mercaptobenzthiazolyl: yl, 41.89-42.64 ppm) [22].

The formation of the complexes CpRu(L)SR [L = dppm](2), dppe (3)] were achieved by the one-pot reaction of CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl, thiolato anions and excess L ligands in refluxing THF for 4 h (Scheme 1) as reported for analogous reactions [19,22,28]. Complexes 2 and 3 are less air sensitive than 1. The <sup>1</sup>H NMR spectra of 2 and 3 display a singlet (for 2: 4.90–4.92 ppm and for 3: 4.68–4.72 ppm) for the Cp-proton resonances. These signals are downfield shifted compared to those of 1 and upfield shifted compared to those of CpRu(L)SR (SR = 2-mercaptobenzimidazolyl, 2-mercaptobenzoxazolyl, 2-mercaptobenzthiazolyl, L = dppm: 5.07-5.13, dppe: 5.00-5.04 ppm) [22]. The resonances of the protons of the heterocyclic thiolato group of complexes 2 and 3 appear as three sets, each set as a doublet of doublet in the range of 6.20–6.52 ppm. The methylene protons of the dppm ligand in 2 appear as two multiplets (due to coupling to each other and to both P-atoms) because they are diastereotopic protons. The phenyl protons are observed as multiplets in the aromatic region. The <sup>31</sup>P NMR spectra for complexes 2 showed a single peak in the range of 17.63-17.65 ppm. The corresponding peaks of **3** lie in the range of 84.99-85.90 ppm. These peaks are also low-field shifted compared to those for cyclopentadienyl thiolato complexes CpRu(dppm)SR (14.20-15.80 ppm) [19,21], and to CpRu(L)SR (SR = 2-mercaptobenzimidazolyl, 2-mercaptobenzoxazolyl, 2-mercaptobenzthiazolyl, L = dppm: 14.20–14.69, dppe: 81.08–81.38 ppm) [22].

# 2.2. Crystal structure of 3b

Fig. 1 shows the ORTEP drawing of two crystallographically independent molecules of **3b** with selected bond lengths and bond angles. The Ru-C bonds of the Cp-ligand ranging from 2.210(6) to 2.240(6) Å are similar to those observed for the analogous CpRu-containing complexes, (e.g. CpRu(dppe)SCO<sub>2</sub>Bu<sup>n</sup>: 2.200(2)–2.240(2) Å, CpRu-(PPh<sub>3</sub>)<sub>2</sub>SCO<sub>2</sub>Bu<sup>n</sup>: 2.202(2)–2.230(2) Å) [29]. The Ru–S distances in **3b** [2.4357(15) and 2.4287(16) Å] lie within the range found for the complexes CpRu(L)(L')SX (X = SSiPr<sup>i</sup><sub>3</sub>, SC=CPh, SCOCH<sub>2</sub>Ph) [30,25,31]. The Ru–P bond



Fig. 1. ORTEP drawing of CpRu(dppe)SThi (**3b**) with atom numbering scheme and thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ru1–C27 2.240(6), Ru1–C28 2.225(6), Ru1–C29 2.230(6), Ru1–C30 2.218(6), Ru1–C31 2.240(6), Ru1–P1 2.2796(16), Ru1–P2 2.2688(15), Ru1–S1 2.4357(15), S1–C35 1.766(7); S2–C35 1.721(9), S2–C32 1.689(9) Å, P1–Ru–P2 83.33(5), P1–Ru1–S1 90.66(5), P2–Ru1–S1 83.65(5), Ru1–S1–C35 110.6(2), S1–C35–S2 122.0(6), S1–C35–C34 128.8(10), S2–C35–C34 108.7(8)°, Ru2–C62 2.219(6), Ru2–C63 2.231(6), Ru2–C64 2.232(6), Ru2–C65 2.210(6), Ru2–C66 2.218(6), Ru2–P3 2.2612(17), Ru2–P4 2.2856(16), Ru2–S3 2.4287(16), S3–C70 1.771(7); S4–C70 1.743(7), S4–C67 1.702(8) Å, P3–Ru2–P4 83.39(6), P3–Ru2–S3 84.00(6), P4–Ru2–S3 92.10(6), Ru2–S3–C70 109.2(2), S3–C70-S4 120.5(4), S3–C70–C69 129.3(6), S4–C70–C69 109.0(5)°.

lengths in **3b** [2.2796(16), 2.2688(15), 2.2612(17) and 2.2856(16) Å] are comparable to those of CpRu(dppe)SCO<sub>2</sub>-Bu<sup>*n*</sup> [2.2736(5), 2.2830(5) Å] [29] and CpRu(dppe)SSO<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>Cl (2.2749(15), 2.2885(18) Å) [32]. The angles of the three legged structure of **3b** are as follows: S1-Ru1-P1 = 90.66(5), S1-Ru1-P2 = 83.65(5), S3-Ru2-P3 = 84.00(6), S3-Ru2-P4 = 92.10(6), P3-Ru2-P4 = 83.39(6) and P1-Ru1-P2 = 83.33(5)°. These data are similar to those found in CpRu(dppm)SX complexes indicating a distorted octahedral geometry around the Ru-center.

# 3. Experimental

# 3.1. General

All manipulations were performed in dry solvents under nitrogen atmosphere by using standard Schlenk techniques. Hexane and tetrahydrofuran were dried over sodium-benzophenone and ethanol by using sodium. Ruthenium chloride hydrate, thiophene, furan, triphenylphosphine, bis(diphenylphosphino)ethane and bis(diphenylphosphino)methane were obtained from Across and were used without any further purification. The reagent CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl was prepared as previously described [33].

Melting points were measured on a smart melting point apparatus and were uncorrected. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker-Avance 400 MHz spectrometer at 400 MHz and 161.3 MHz, respectively. All chemical shifts are quoted in ppm downfield of TMS (<sup>1</sup>H) or 85% phosphoric acid (<sup>31</sup>P) and referenced using the chemical shifts of residual solvent resonances. Elemental analyses were performed at the Institute of Organic and Macromolecular Chemistry, FSU-Jena, Germany.

# 3.2. General procedure for the preparation of $CpRu(PPh_3)_2SR$ , 1

A 100 mL Schlenk flask equipped with a reflux condenser was charged with 50 mL of THF and  $CpRu(PPh_3)_2Cl$ (0.50 g, 0.72 mmol). A freshly prepared solution of the thiolato anions (1.0 mmol) was added and the resulting mixture was refluxed for 1 h. The solvent was removed under vacuum to about 2 mL and then 50 mL of hexane was added. On standing at 4 °C overnight the solution produced an orange-brown solid which was separated by filtration, washed several times with cold hexane and dried in vacuum.

# 3.2.1. CpRu(PPh<sub>3</sub>)<sub>2</sub>SFu 1a

Yield: 70%. M.p.: 93–94 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.17 (s, 5H, Cp), 6.80 (dd, 1H, C<sub>4</sub>H<sub>3</sub>O, <sup>3</sup>J = 3.4 Hz, <sup>4</sup>J = 1.1 Hz), 6.98 (m, 18H, PPh<sub>3</sub>), 7.52 (m, 12H, PPh<sub>3</sub>), 7.79 (m, 2H, C<sub>4</sub>H<sub>3</sub>O). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  44.55. *Anal.* Calc. for C<sub>45</sub>H<sub>38</sub>OP<sub>2</sub>RuS: C, 68.43; H, 4.85; S, 4.06. Found: C, 67.87; H, 4.65; S, 3.85%.

# 3.2.2. CpRu(PPh<sub>3</sub>)<sub>2</sub>SThi 1b

Yield: 82%. M.p.: 117–119 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.15 (s, 5H, Cp), 6.79 (dd, 1H, C<sub>4</sub>H<sub>3</sub>S, <sup>3</sup>J = 3.6 Hz, <sup>4</sup>J = 1.0 Hz), 6.96 (m, 18H, PPh<sub>3</sub>), 7.52 (m, 12H, PPh<sub>3</sub>), 7.76 (m, 2H, C<sub>4</sub>H<sub>3</sub>S). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  44.54. *Anal.* Calc. for C<sub>45</sub>H<sub>38</sub>P<sub>2</sub>RuS<sub>2</sub>: C, 67.06; H, 4.75; S, 7.96. Found: C, 66.45; H, 4.58; S, 7.87%.

# 3.3. General procedure for the Preparation of CpRu(L)SR,2, 3

A 100 mL Schlenk flask equipped with a reflux condenser was charged with 50 mL THF,  $CpRu(PPh_3)_2Cl$ (0.50 g, 0.72 mmol) and bis(diphenylphosphino)alkane (1.00 mmol). A freshly prepared solution of the thiolato anions (1.00 mmol) was added. The resulting mixture was refluxed for 4 h. The volatiles were removed under vacuum and the remaining solid was extracted with toluene  $(3 \times 5.0 \text{ mL})$ . The extracts were combined and concentrated under vacuum to about 4.0 mL. Addition of 30 mL of cold hexane led to the deposition of an orange solid, which was collected by removing the mother liquor and recrystallized from THF/hexane.

# 3.3.1. CpRu(dppm)SFu 2a

Yield = 70%. M.p.: 181–183 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.72 (m, 1H, PCH<sub>2</sub>), 4.75 (m, 1H, PCH<sub>2</sub>), 4.92 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.32 (dd, 1H, C<sub>4</sub>H<sub>3</sub>O, <sup>3</sup>*J* = 3.2 Hz, <sup>4</sup>*J* = 1.0 Hz), 6.45 (dd, 1H, C<sub>4</sub>H<sub>3</sub>O, <sup>3</sup>*J* = 3.2 Hz, <sup>3</sup>*J* = 5.3 Hz), 6.52 (dd, 1H, C<sub>4</sub>H<sub>3</sub>O, <sup>3</sup>*J* = 5.3 Hz, <sup>4</sup>*J* = 1.0 Hz), 7.08 (m, 12H, PPh<sub>2</sub>), 7.50 (m, 8H, PPh<sub>2</sub>). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  17.63. *Anal.* Calc. for C<sub>34</sub>H<sub>30</sub>OP<sub>2</sub>RuS: C, 62.86; H, 4.65; S, 4.94. Found: C, 62.49; H, 4.74; S, 5.05%.

# 3.3.2. CpRu(dppm)SThi 2b

Yield = 72%. M.p.: 171–173 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.68 (m, 1H, PCH<sub>2</sub>), 4.70 (m, 1H, PCH<sub>2</sub>), 4.90 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.30 (dd, 1H, C<sub>4</sub>H<sub>3</sub>S, <sup>3</sup>*J* = 3.4 Hz, <sup>4</sup>*J* = 0.9 Hz), 6.41 (dd, 1H, C<sub>4</sub>H<sub>3</sub>S, <sup>3</sup>*J* = 3.4 Hz, <sup>4</sup>*J* = 5.6 Hz), 6.50 (dd, 1H, C<sub>4</sub>H<sub>3</sub>S, <sup>3</sup>*J* = 5.6 Hz, <sup>4</sup>*J* = 0.9 Hz), 7.03 (m, 12H, PPh<sub>2</sub>), 7.53 (m, 8H, PPh<sub>2</sub>). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  17.65. *Anal.* Calc. for C<sub>34</sub>H<sub>30</sub>P<sub>2</sub>RuS<sub>2</sub>: C, 61.34; H, 4.54; S, 9.63. Found: C, 61.50; H, 4.60; S, 9.38%.

## 3.3.3. CpRu(dppe)SFu 3a

Yield = 90%. M.p.: 142–144 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 1.83 (m, 2H, PCH<sub>2</sub>), 2.70 (m, 2H, PCH<sub>2</sub>), 4.68 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.85 (dd, 1H, C<sub>4</sub>H<sub>3</sub>O, <sup>3</sup>J = 3.2 Hz, <sup>4</sup>J = 1.0 Hz), 6.22 (dd, 1H, C<sub>4</sub>H<sub>3</sub>O, <sup>3</sup>J = 3.2 Hz, <sup>3</sup>J = 5.5 Hz), 6.43 (dd, 1H, C<sub>4</sub>H<sub>3</sub>O, <sup>3</sup>J = 5.5 Hz, <sup>4</sup>J = 1.0 Hz), 6.90 (m, 12H, PPh<sub>2</sub>), 7.79 (m, 8H, PPh<sub>2</sub>). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  85.90. *Anal.* Calc. for C<sub>35</sub>H<sub>32</sub>OP<sub>2</sub>RuS: C, 63.34; H, 4.86; S, 4.83. Found: C, 63.25; H, 4.76; S, 4.91%.

## 3.3.4. CpRu(dppe)SThi 3b

Yield = 85%. M.p.: 224–225 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.30 (m, 2H, PCH<sub>2</sub>), 2.80 (m, 2H, PCH<sub>2</sub>), 4.72 (s, 5H, Cp), 5.90 (dd, 1H, C<sub>4</sub>H<sub>3</sub>S, <sup>3</sup>J = 3.4 Hz, <sup>4</sup>J = 1.0 Hz), 6.20 (dd, 1H, C<sub>4</sub>H<sub>3</sub>S, <sup>3</sup>J = 3.4 Hz, <sup>3</sup>J = 5.4 Hz), 6.50 (dd, 1H, C<sub>4</sub>H<sub>3</sub>S, <sup>3</sup>J = 5.4 Hz, <sup>4</sup>J = 1.0 Hz), 7.12 (m, 12H, PPh<sub>2</sub>); 7.66 (m, 8H, PPh<sub>3</sub>). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  84.99. *Anal.* Calc. for C<sub>35</sub>H<sub>32</sub>P<sub>2</sub>RuS<sub>2</sub>: C, 61.84; H, 4.74; S, 9.43. Found: C, 61.67; H, 4.91; S, 8.71%.

# 3.4. Crystallographic analysis of CpRu(dppe)SThi 3b

Single crystals suitable for X-ray structure determination were obtained by re-crystallization of **3b** from THF/hexane mixture. X-ray diffraction measurements were performed on X8APEXII CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å at 100(2) K. The crystal data for **3b** are shown in Table 1. The crystal was positioned at 40 mm from the detector and 1390 frames were measured, each for 40 s over 1° scan width. The data were processed using SAINT software [34]. Intensity data were cor-

| Table | 1 |
|-------|---|
|       |   |

Selected crystal data and refinement parameters for CpRu(dppe)SThi, 3b

| Empirical formula                | $C_{35}H_{32}P_2RuS_2$                                       |
|----------------------------------|--|
| Crystal system                   | monoclinic   |
| Volume (Å <sup>3</sup> )         | 5875.0(5)  |
| Unit cell dimensions             |  |
| a (Å)                            | 29.7494(16)  |
| b (Å)                            | 10.6068(5)   |
| <i>c</i> (Å)                     | 19.4659(9)   |
| β (°)                            | 106.969(3)   |
| Formula weight (g/mol)           | 679.74   |
| Density (Mg/m <sup>3</sup> )     | 1.537  |
| λ (Å)                            | 0.71073  |
| $\mathbf{R}[F^2 > 2\sigma(F^2)]$ | 0.0571   |
| Crystal size (mm)                | 0.18 	imes 0.16 	imes 0.12                                   |
| Space group                      | $P2_1/c$   |
| Ζ                                | 4  |
| Index range                      | $-35 \leq h \leq 35, -12 \leq k \leq 12, -23 \leq l \leq 23$ |
| Goodness-of-fit                  | 1.081  |
| Radiation type                   | Μο Κα  |
| $\mu (\mathrm{mm}^{-1})$         | 0.810  |
| θ (°)                            | 2.19-25.00   |
| $\omega R(F^2)^{\rm a}$          | 0.1556   |

<sup>a</sup>  $\omega = 1/[\sigma^2(F_o^2) + (0.0598P)^2]$  where  $P = (F_o^2 + 2F_o^2)/3$ .

rected for absorption using intensities of redundant reflections. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed in geometrically calculated positions and refined as riding atoms in the subsequent least-squares model refinements. The isotropic thermal parameters were estimated to be 1.2 times the values of the equivalent isotropic thermal parameters of the atoms to which hydrogens were bonded. The following computer programs were used: structure solution, SHELXS-97 [35] refinement, SHELXL-97 [36] molecular diagrams, ORTEP [37] scattering factors were taken from the literature [38]. The thiophene unit in the first crystallographically independent molecule was found to be disordered over two positions with occupation ratio about 80:20. The corresponding atoms of the two split parts were refined with restrained geometry using SADI instruction of SHELXL-97. The thermal displacement parameters of two atoms (C32X and C34X) were refined using ISOR instruction. Attempts to split the phenyl ring C44–C49 in two positions failed.

#### 4. Supplementary material

CCDC 652224 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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