



# Bimetalamacrocycles involving tetrakis(diphenylphosphinoalkylthio) tetrathiafulvalene

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## ABSTRACT

Two novel tetrathiafulvalene (TTF) ligands, substituted by four diphenylphosphinoalkylthio groups, have been synthesized and characterized. Their redox properties, determined by cyclic voltammetry, have been compared with their precursors and discussed. The ability of these redox active ligands to react with two equivalent of  $cis\text{-W}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$  is presented. X-ray crystal structure of a bis 13-metallamacrocycle is reported together with its redox behaviour.

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## 1. Introduction

Formation of large metallamacrocycles based on transition metal complexes with diphosphine ligands remains an important synthetic challenge [1]. One of the strategies developed to reach such compounds involves the coordination of a bidentate  $\alpha,\omega$ -diphosphine ligand to the transition metal center [1]. Note however that with this approach, most of the  $\alpha,\omega$ -diphosphine ligands with a flexible backbone between the two phosphorus atoms are more likely to bridge two metals rather than to form a chelate ring affording oligomeric or polymeric structures [2]. Association of an electroactive ligand such as a tetrathiafulvalene core (TTF) and transition metals within a metallamacrocycle has been scarcely described so far [3,4] even if TTF has been incorporated in various molecular and supramolecular systems [5]. In continuation of our work on the formation of hybrid organic–inorganic building blocks using mono [6] and bis phosphino-TTF [7] as the electroactive ligand, we decided to investigate the formation of large bimetalcycles using tetrakis substituted (diphenylphosphinoalkylthio)-TTF as starting material. Indeed, we have recently described the formation of redox active 17- and 19-membered metallamacrocycles thanks to the chelating ability of bis(diphenylphosphinoalkylthio)-TTF towards  $\text{M}(\text{CO})_4$  fragments ( $\text{M} = \text{Mo}, \text{W}$ ) (Chart 1) [7]. It is worth mentioning that due to (i) the possible *cis/trans* isomerization of the TTF core, (ii) the possible *cis/trans* coordination of the two P atoms around the metallic fragment and (iii) the *trans* TTF as an element of planar chirality, six stereoisomers were obtained [7].

Therefore, we decided to investigate the behaviour of tetrakis substituted (diphenylphosphinoalkylthio)-TTF towards  $\text{W}(\text{CO})_4$  fragments and their ability to form metallamacrocycles using alkyl chain of similar length as the ones involved in the formation of the 17- and 19-membered metallamacrocycles [7]. Two types of metallamacrocycles can be envisioned starting from these tetra substituted TTF (Chart 2), either the phosphino groups coordinate the tungsten atom in a similar way as the one observed from the bis substituted TTF, to afford a bis 17- or 19-membered metallamacrocycles (way a), or two phosphino groups on the same dithiole ring coordinate the metallic fragment (way b). Herein, we report the synthesis of the tetrakisphosphino ligand **1** and **2** where the phosphine moieties are linked to the donor core through a thiopropyl or a thiobutyl alkyl chain and the influence of this alkyl chain on the formation of the metallamacrocycles.

## 2. Results and discussion

The synthesis of the ligands **1** and **2** was realized according to the chemical pathway depicted in Scheme 1 starting from the tetrakis(cyanoethylthio)-TTF **3** [8]. Deprotection of the thiolate was achieved in DMF using a base such as cesium carbonate at 70 °C during 3 h instead of the cesium hydroxide usually used for this type of deprotection. Indeed, it has to be mentioned that the use of cesium hydroxide lead to a mixture of mono, bis and tetradeprotected derivatives. In order to prepare the tetrakis(diphenylphosphinopropylthio)-TTF **1** we added 3-iodopropylphosphine-borane in the medium while for the synthesis of tetrakis(diphenylphosphinobutylthio)TTF **2**, 4-bromobutylphosphine-borane was added [9]. The tetrakis(phosphine borane)-TTFs **4** and **5** were obtained as air

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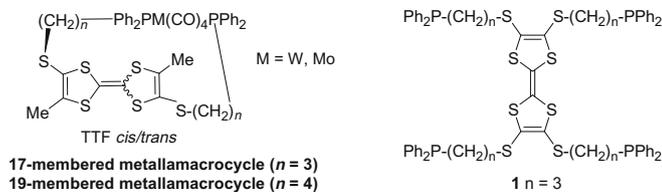


Chart 1.

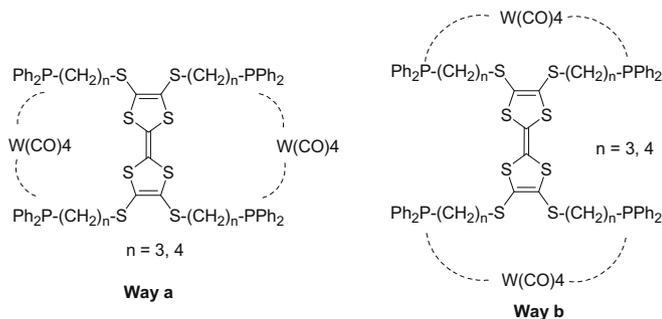


Chart 2.

stable derivatives in 73% and 68% yield, respectively. Deprotection of the phosphines was realized by heating a solution of the tetrakis(phosphineborane)-TTF **4** and **5** in toluene under inert atmosphere at 50 °C for 5 h in the presence of four equivalents of DABCO. After filtration on celite, the tetrakis(diphenylphosphinoalkylthio)-TTF **1** and **2** were obtained in 71% and 68% yield, respectively. Note that these derivatives **1** and **2** are easily transformed, upon air exposure, into the corresponding phosphine oxides. Therefore, deprotection of the phosphine was performed in order to be characterized by  $^1\text{H}$  and  $^{31}\text{P}$  NMR these TTFs and to analyze their redox properties.

The influence of the substituents on the redox properties of the TTFs **1–5** has been studied by cyclic voltammetry. The oxidation peak potentials of the various TTFs are collected in Table 1. In both series it can be noticed that the effect of the diphenylphosphineborane group or the diphenylphosphine one decreases with the length of the alkyl chain. Indeed, in both cases, the butyl derivatives, TTF **2** and **5**, are easier to oxidize than the propyl derivatives, TTF **1** and **4**. However the electron withdrawing effect of these two groups is less important than the one of the cyanoethyl group. The lack of reversibility observed for the TTFs **1** and **2** was attributed to the presence of the phosphines substituents and to their reducing character towards the generated mono and biscationic species in the medium.

In order to form metal carbonyl complexes with these TTF ligands, we used  $\text{cis-W}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$  where the two labile piperi-

Table 1

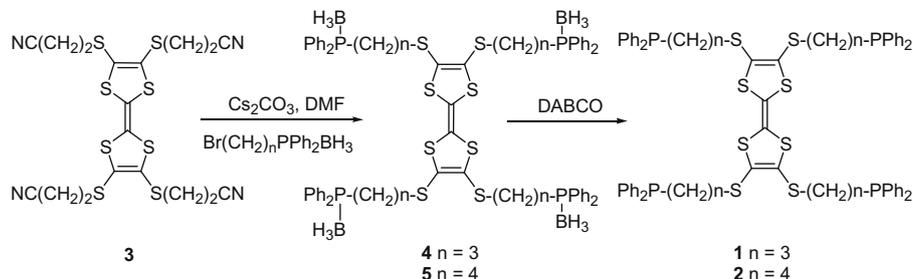
Oxidation peak potentials in V vs. SCE, Pt working electrode and  $^{31}\text{P}$  chemical shifts in  $\text{CDCl}_3$  for compounds **1–6**.

TTF(SR) <sub>4</sub>	$\delta^{31}\text{P}$ ppm	TTF-(SR) <sub>4</sub>	$E_{\text{pa}}^1/E_{\text{pc}}^1$	$E_{\text{pa}}^2/E_{\text{pc}}^2$
R, compound				
–(CH <sub>2</sub> ) <sub>3</sub> –PPh <sub>2</sub> <b>1</b>	–16.7		0.61 <sup>*</sup>	0.86 <sup>*</sup>
–(CH <sub>2</sub> ) <sub>4</sub> –PPh <sub>2</sub> <b>2</b>	–16.4		0.58 <sup>*</sup>	0.84 <sup>*</sup>
–(CH <sub>2</sub> ) <sub>2</sub> –CN <b>3</b>			0.71/0.63	0.99/0.88
–(CH <sub>2</sub> ) <sub>3</sub> –PPh <sub>2</sub> BH <sub>3</sub> <b>4</b>	15.9		0.59/0.51	0.95/0.87
–(CH <sub>2</sub> ) <sub>4</sub> –PPh <sub>2</sub> BH <sub>3</sub> <b>5</b>	15.9		0.55/0.49	0.90/0.82
Metallamacrocycle <b>6</b>	8		0.62/0.54	0.97 <sup>*</sup>

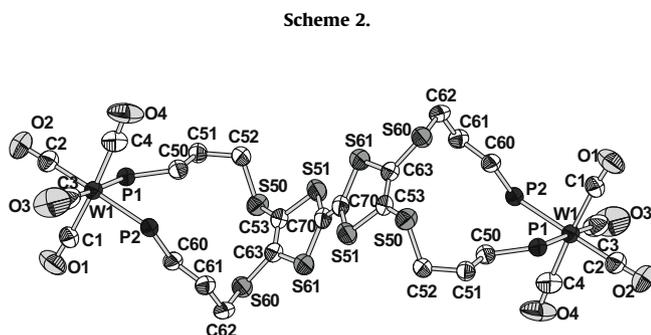
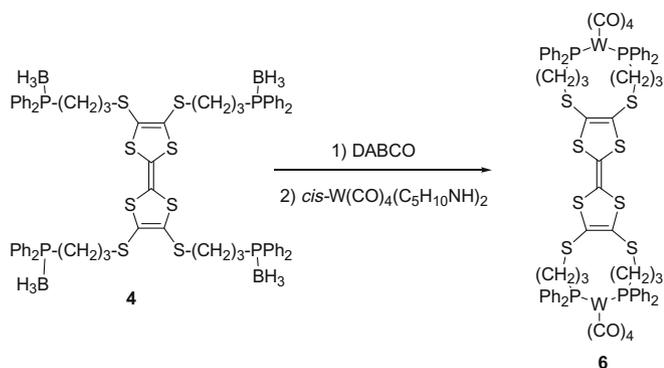
<sup>\*</sup> Irreversible process.

dino ligands can be replaced by other ligands such as two diphenyl phosphino moieties [10]. As mentioned earlier, for mono and bis substituted phosphino-TTF derivatives, the metal carbonyl complexation can be realized, directly from the phosphine-borane TTF complexes [6,7], in a one-pot procedure by a two-step chemical synthesis: (i) decomplexation of the phosphine borane and (ii) addition of  $\text{cis-W}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$  in the medium. Using this one-pot procedure, one avoids any undesired oxidation of the phosphine groups. According to this strategy, we first studied TTF **1** as starting material and deprotected the phosphine groups by heating TTF **1** in the presence of four equivalents of DABCO at 50 °C for 4 h in dry and degassed toluene. Addition of two equivalents of  $\text{cis-W}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$  in the medium followed by the heating of the solution for 2 h at 90 °C allowed us to isolate after column chromatography upon silica gel, besides polymeric derivatives, one compound in 33% yield. Analysis of this compound by  $^{31}\text{P}$  NMR in  $\text{CDCl}_3$  reveals one singlet at 8 ppm associated with a small doublet due to the coupling of the phosphorus atom with the  $^{183}\text{W}$  isotope. The presence of only one singlet suggests the formation of a symmetrical molecule and the coupling constant observed  $J_{\text{PW}}^1 = 231$  Hz is characteristic for the presence of *cis*-P–W–P isomer [11,12]. Slow diffusion of methanol into a dichloromethane solution of this derivative allowed us to obtain crystals suitable for X-ray structure analysis. The crystal structure determination reveals that a bimetallic complex is formed and that two 13-membered metallamacrocycles are formed and connected by the TTF core (way b, Chart 2), as the two phosphine groups on one dithiole ring of the TTF are coordinated to the metal center (Scheme 2). This complex **6** crystallizes in the monoclinic system, space group  $P2_1/n$  with the complex located on an inversion center and one  $\text{CH}_2\text{Cl}_2$  molecule in general position. The molecular structure of this bimetallic compound **6** is represented in Figs. 1 and 2 and selected bond lengths and angles are listed in Table 2.

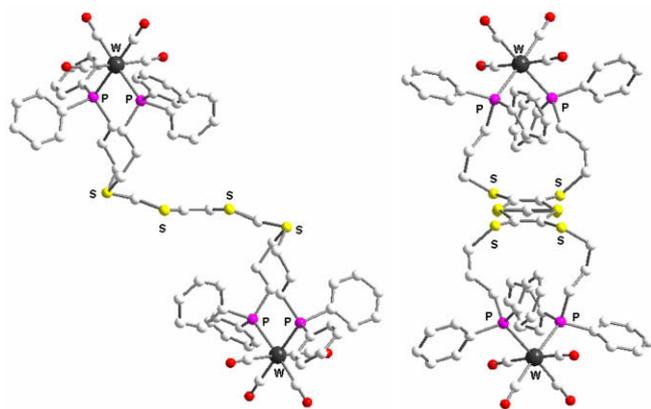
Within this complex, the phosphines are *cis* coordinated to the metal center and this confirms the *cis*-P–W–P structure deduced from the  $^{31}\text{P}$  NMR spectrum. The TTF moiety is not planar and the dithiole rings are folded along the S...S vector with an angle of 20° and adopts a chair conformation. Analysis of the bond lengths of the TTF core shows that the TTF is under the neutral



Scheme 1.



**Fig. 1.** ORTEP view of TTF complex **6** showing the atom labeling (50% probability ellipsoids). Phenyl rings and hydrogen atoms are omitted for clarity.

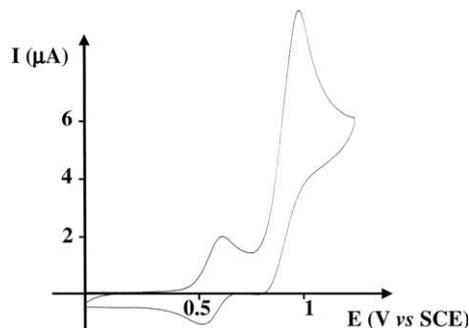


**Fig. 2.** Side views of TTF complex **6** showing the steric hindrance around the TTF core. Hydrogen atoms are omitted for clarity.

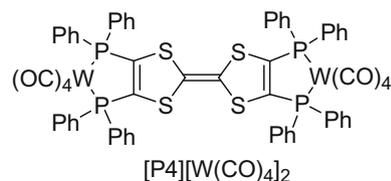
**Table 2**  
Selected bond lengths (Å) and angles (°) for complex **6**.

Bond lengths			
P1–W1	2.5424(15)	C1–O1	1.141(7)
P2–W1	2.5377(14)	C2–O2	1.162(7)
W1–C1	2.021(6)	C3–O3	1.153(8)
W1–C2	1.983(6)	C4–O4	1.145(8)
W1–C3	1.966(7)	C70–C70	1.346(12)
W1–C4	2.016(7)		
Bond angles			
P2–W1–P1	94.11(5)	C53–C63–S60	122.9(4)
C60–P2–W1	116.62(18)	C63–C53–S50	123.9(4)
C50–P1–W1	116.68(17)		

state. As seen in Table 2, The W–P distances and P–W–P interligand angles are in the usual range for non cyclic bisdiphenylphosphine



**Fig. 3.** Cyclic voltammogram of complex **6**.



**Chart 3.**

derivatives coordinated to  $W(CO)_4$  fragment [13], which indicates that the two 13-membered metallamacrocycles are not constrained. No short S...S contacts are observed between neighboring complex **6** in the solid state presumably due to the huge steric hindrance of the two metallacycles fused to the TTF core (Fig. 2).

It is interesting to note that using TTF **2**, with the longer butyl arms, as starting material and following the same experimental procedure, that is decomplexation of the phosphine and addition of two equivalents of  $cis\text{-}W(CO)_4(C_5H_{10}NH)_2$  in the medium, we did not isolate a monomeric structure. Instead, analysis by  $^{31}P$  NMR, of the different fractions obtained after chromatographic separation, reveals the presence of numerous signals attributed to polymeric derivatives resulting from presumably intra and intermolecular complexation.

The redox properties of the bis(13-membered metallacycle) **6** obtained from **1** was studied by cyclic voltammetry. Two oxidation waves are observed, the first one is reversible and corresponds to the oxidation of the TTF in its radical cation while the second process is not fully reversible (Fig. 3). Actually, the latter is due to the concomitant oxidation of TTF radical cation into the dication and the oxidation of the two metallic centers. This process is not fully reversible due to the loss of carbonyl ligands on the metallic center. It is interesting to note that, due to the presence of the propylthio spacer group, the first redox potential of the TTF is not modified by the presence of the two  $W(CO)_4$  fragments coordinated to the phosphino groups. This result strongly differs from what was observed with the tetrakis(diphenylphosphino)TTF, noted P4, in the bimetallic  $[P4][W(CO)_4]_2$  where the phosphorus atoms are directly linked to the donor core (Chart 3) [12]. In this case a strong anodic shift of the first oxidation is observed (+400 mV) due to strong interactions between the TTF core and the metallic fragment.

### 3. Conclusions

In summary, we described the synthesis of a novel family of tetradentate phosphino-TTFs where the phosphino moieties are linked to the donor core through a propylthio or a butylthio spacer group. Depending on the length of this spacer, a dinuclear tungsten complex has been formed, as evidenced by X-ray structure analysis,

through the coordination of the two phosphino groups on the same dithiole ring to a metallic  $W(CO)_4$  fragment. The redox properties of this electroactive bis 13-membered metallamacrocycles were determined and comparison with those of the starting ligand shows that the presence of these two metallamacrocycles does influence the electron donating ability of the TTF.

## 4. Experimental

### 4.1. General

$^1H$  NMR and  $^{31}P$  NMR spectra were recorded on Bruker AC 300P or ARX 200 spectrometers. Chemical shifts are reported in ppm referenced to TMS for  $^1H$  NMR and to  $H_3PO_4$  for  $^{31}P$  NMR. Melting points were measured using a Kofler hot stage apparatus. Mass spectra were performed by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Methanol was distilled from calcium and dichloromethane from  $P_2O_5$ . Chromatography was performed using silica gel Merck 60 (70–260 mesh). The tetrakis(cyanoethylthio)-TTF **3** was prepared according to previously published procedures [8]. *Cis*- $W(CO)_4(NC_5H_{11})_2$  was prepared from  $W(CO)_6$  according to published procedure [10]. Cyclic voltammetry were carried out on a  $10^{-3}$  M solution of the derivatives in dichloromethane, containing a 0.1 M  $nBu_4NPF_6$  as the supporting electrolyte. Voltammograms were recorded at  $0.1 V s^{-1}$  at a platinum disk electrode ( $A = 1 mm^2$ ). The potentials were measured versus Saturated Calomel Electrode.

### 4.2. Synthesis and characterization

#### 4.2.1. 2,3,6,7-Tetrakis[4-(boronatodiphenylphosphino)alkylthio]tetrathiafulvalene 4 and 5

To a solution of tetrakis(cyanoethylthio)-TTF **3** (400 mg, 0.73 mmol) in 20 mL of DMF was added under argon a solution of  $Cs_2CO_3$ ,  $H_2O$  (410 mg, 2.4 mmol). The mixture was allowed to stir for 3 h at 70 °C after which, 3-iodopropylidiphenylphosphineborane (1 g, 3.65 mmol) for **4** or 4-bromobutylidiphenylphosphineborane (1.2 g, 3.6 mmol) for **5** was added. The mixture was stirred for 12 h and then the solvents were evaporated. The residue was extracted with  $CH_2Cl_2$  and washed with water. The organic layer was dried over  $Na_2SO_4$  and evaporated. Chromatography over silica gel (4:1  $CH_2Cl_2/PE$ ) afforded **4** (690 mg, 73%) as an orange powder or **5** as an orange thick oil (670 mg, 68%).

TTF **4** mp 82 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  0.2–1.8 (m, 12H); 1.85 (m, 8H); 2.30 (m, 8H); 2.90 (t,  $J = 7.1$  Hz, 8H); 7.30–7.70 (m, 40H);  $^{31}P$  NMR (121 MHz,  $CDCl_3$ )  $\delta$  15.9; HRMS: Calc. for  $C_{66}H_{76}B_4P_4S_8$  1292.3036. Found 1292.3046.

TTF **5**  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  0.2–1.6 (m, 12H); 1.65 (m, 16H); 2.15 (m, 8H); 2.75 (t,  $J = 7.1$  Hz, 8H); 7.30–7.80 (m, 40H);  $^{31}P$  NMR (121 MHz;  $CDCl_3$ )  $\delta$  15.8; HRMS: Calc. for  $C_{70}H_{84}B_4P_4S_8$  1348.3700. Found 1348.3724.

#### 4.2.2. 2,3,6,7-Tetrakis[3-diphenylphosphinoalkylthio]tetrathiafulvalene 1 and 2

This procedure was realized in order to characterize by  $^1H$  and  $^{31}P$  NMR the TTF **1** and **2**. The typical procedure is as followed. To a solution of TTF **4** or **5** (0.1 mmol) in 10 ml of dried, degassed toluene was added under argon DABCO (0.4 mmol). The mixture was stirred for 4 h at 50 °C after which the solution was filtered through a silica gel column under inert atmosphere using dry and degassed toluene as eluent. TTF **1**  $^1H$  NMR (200 MHz;  $CDCl_3$ )  $\delta$  1.75 (m, 8H); 2.32 (m, 8H); 2.80 (t,  $J = 7.1$  Hz, 8H); 7.30–7.70 (m, 40H);  $^{31}P$  NMR (121 MHz;  $CDCl_3$ )  $\delta$  –16.7. TTF **2**  $^1H$  NMR (200 MHz;  $CDCl_3$ )  $\delta$  1.55 (m, 8H); 1.72 (m, 8H); 2.08 (m, 8H); 2.80 (t,  $J = 7.0$  Hz, 8H); 7.20–7.50 (m, 40H);  $^{31}P$  NMR (121 MHz;  $CDCl_3$ )  $\delta$  –16.4.

**Table 3**

Crystal data and structure refinement parameters for complex **6**.

Structure parameter	(Complex <b>6</b> ), $(CH_2Cl_2)_2$
Empirical formula	$C_{76}H_{68}Cl_4O_8P_4S_8W_2$
Molecular weight	1999.16
Cryst system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.278(5)
b (Å)	19.724(5)
c (Å)	20.301(5)
$\alpha$ (°)	90
$\beta$ (°)	94.707(5)
$\gamma$ (°)	90
V (Å <sup>3</sup> )	4102(2)
T (K)	293(2)
Z	2
Dcalc (g/cm <sup>3</sup> )	1.619
$\mu$ (mm <sup>-1</sup> )	3.266
Total reflections	16 664
Unique data ( $R_{int}$ )	9377(0.0282)
Obs reflections ( $I > 2\sigma(I)$ )	8003
$R_1, wR_2$	0.0448, 0.1074
$R_1, wR_2$ (all data)	0.0543, 0.1123
Goodness-of-fit (GoF)	1.139

#### 4.2.3. Complex 6

To a solution of TTF **1** (310 mg, 0.24 mmol) in 25 ml of dried, degassed toluene was added under argon DABCO (110 mg, 0.96 mmol). The mixture was stirred for 4 h at 50 °C after which *cis*- $W(CO)_4(NHC_5H_{10})_2$  (220 mg, 0.48 mmol) in 8 ml of degassed  $CHCl_3$  was added. Stirring was continued for 2 h at 90 °C and then the solvent was evaporated. The residue was extracted with  $CH_2Cl_2$  and washed with water. The organic layer was dried over  $Na_2SO_4$  and the solvent evaporated. Chromatography over silica gel (1:1  $CH_2Cl_2/PE$ ) gave the complex **6** as an orange powder in 33% yield. Mp = 165 °C(dec);  $^1H$  NMR (200 MHz;  $CDCl_3$ ) 1.75 (m, 8H); 2.35 (m, 8H); 2.85 (t,  $J = 7.0$  Hz, 8H); 7.30–7.50 (m, 40H);  $^{31}P$  NMR (121 MHz;  $CDCl_3$ )  $\delta$  8.0 ( $J_{PW}^1 = 231$  Hz); IR (cm<sup>-1</sup>) $\nu_{C=O}$  1872, 1884, 1907, 2013; HRMS: Calc. for  $C_{74}H_{64}O_8P_4S_8W_2$ : 1828.0337. Found: 1828.0280.

### 4.3. Crystallography

Single-crystal diffraction data were collected on Nonius KappaCCD diffractometer (Centre de Diffractométrie X, Université de Rennes, France). Details of the crystallographic are given in Table 3.

## Appendix A. Supplementary material

CCDC 723837 contains the supplementary crystallographic data for complex **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.04.006](https://doi.org/10.1016/j.jorganchem.2009.04.006).

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