Inorganica Chimica Acta 363 (2010) 1611-1614

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# Carbon–hydrogen bond activation of phenyldi(2-thienyl)phosphine at a triosmium cluster centre

Shishir Ghosh<sup>a</sup>, Graeme Hogarth<sup>b</sup>, Derek A. Tocher<sup>b</sup>, Ebbe Nordlander<sup>c</sup>, Shariff E. Kabir<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh

<sup>b</sup> Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

<sup>c</sup> Inorganic Chemistry Research Group, Chemical Physics, Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, SE-22100 Lund, Sweden

## ARTICLE INFO

Article history: Received 25 November 2009 Accepted 22 January 2010 Available online 29 January 2010

Keywords: Triosmium clusters Phenyldi(2-thienyl)phosphine Carbon–hydrogen bond activation X-ray structures

#### ABSTRACT

The phenyldi(2-thienyl)phosphine (PhPTh<sub>2</sub>) complexes  $[Os_3(CO)_{12-n}(PhPTh_2)_n]$  (n = 1-3) (1-3) have been prepared. Thermolysis of **1** and either **2** or **3** in octane affords carbon–hydrogen bond activation products  $[Os_3(CO)_9[\mu_3-PPhTh(C_4H_2S)](\mu-H)]$  (**4**) and  $[Os_3(CO)_8(PPhTh_2)[\mu_3-PPhTh(C_4H_2S)](\mu-H)]$  (**5**), respectively. Both exist as isomeric mixtures differing in the relative positions of phenyl and thienyl substituents with respect to the triosmium centre. The nature of the process has been confirmed by a single crystal X-ray diffraction analysis of **4**.

© 2010 Elsevier B.V. All rights reserved.

Inorganica Chimica Acta

# 1. Introduction

The reactivity of thienyl phosphines with transition metal carbonyl clusters continues to of considerable interest since they exhibit a variety of coordination modes and cluster-mediated rearrangements the nature of which has relevance to modeling the industrially important catalytic hydrodesulfurization process [1-9]. In this context, their reactivity with triruthenium and triosmium clusters has been investigated quite thoroughly in recent years. In 1995, Vahrenkamp and co-workers reported that the reaction of tri(2-thienyl)phosphine (PTh<sub>3</sub>) with Ru<sub>3</sub>(CO)<sub>12</sub> gave low yields of both [Ru<sub>3</sub>(CO)<sub>10</sub>(PTh<sub>3</sub>)<sub>2</sub>] and trans-[Ru(CO)<sub>3</sub>(PTh<sub>3</sub>)<sub>2</sub>] in which the ligand acts as a simple tertiary phosphine [5]. In the following year, Deeming and co-workers detailed the reactivity of diphenyl(2-thienyl)phosphine (PPh<sub>2</sub>Th) with Ru<sub>3</sub>(CO)<sub>12</sub> leading to both carbon-hydrogen and carbon-phosphorus bond cleavage and affording complexes containing cyclometalated µ<sub>3</sub>-Ph<sub>2</sub>PC<sub>4</sub>H<sub>2</sub>S and  $\mu_4$ -thiophyne ligands [6]. More recently, we reported the reactivity of  $[Ru_3(CO)_{10}(\mu$ -dppm)] with PTh<sub>3</sub>. This initially affords the simple substitution product  $[Ru_3(CO)_9(PTh_3)(\mu-dppm)]$  which upon mild heating undergoes carbon-hydrogen, carbon-phosphorus and carbon-sulfur bond cleavage to afford the thiophyne cluster  $[Ru_3(CO)_7(\mu-dppm)(\mu_3-\eta^2-C_4H_2S)\{\mu-PTh_2\}(\mu-H)]$  and the thiophyne ring-opened cluster  $[Ru_3(CO)_5(\mu-CO)(\mu-dppm)(\mu_3-\eta^3-\eta^3-\eta^3-\eta^3)]$  $SC_4H_2$  [µ-PTh<sub>2</sub>], the latter being a unique example of an open triruthenium cluster containing a capping 1-thia-1,3-butadiene ligand [7]. In contrast, the reactions of PTh<sub>3</sub> and PPh<sub>2</sub>Th with  $Os_3(CO)_{12}$  and  $[Os_3(CO)_{10}(\mu-H)_2]$  lead to the formation of both simple substitution and metalated products [8,9]. As part of our work on the reactivity of functionalized phosphines with trimetallic clusters, we have studied the reactions of PPhTh<sub>2</sub> with triosmium clusters  $[Os_3(CO)_{12-n}(NCMe)_n]$  (n = 0, 1, 2), the results of which are described herein.

## 2. Experimental

All manipulations were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques. Reagent-grade solvents were dried and distilled by standard methods prior to use. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on Bruker DPX 400 instruments. Elemental analyses were performed by Microanalytical Laboratories, University College London.  $Os_3(CO)_{12}$  was purchased from Strem Chemicals Inc. and used without further purification and the clusters  $[Os_3(CO)_{11}(NCMe)]$  and  $[Os_3(-CO)_{10}(NCMe)_2]$  were prepared according to the literature methods [10].

## 2.1. Reaction of $[Os_3(CO)_{11}(NCMe)]$ with PPhTh<sub>2</sub>

PPhTh<sub>2</sub> (45 mg, 0.164 mmol) was added to a  $CH_2Cl_2$  solution (30 mL) of  $[Os_3(CO)_{11}(NCMe)]$  (151 mg, 0.164 mmol) and the reaction mixture was then stirred at 25 °C for 24 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH<sub>2</sub>Cl<sub>2</sub> (9:1, v/v)



Note

<sup>\*</sup> Corresponding author. E-mail address: skabir\_ju@yahoo.com (S.E. Kabir).

<sup>0020-1693/\$ -</sup> see front matter  $\odot$  2010 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2010.01.030

developed only one band which afforded  $[Os_3(CO)_{11}(PPhTh_2)]$  (1) (165 mg, 87%) as yellow crystals from hexane/CH<sub>2</sub>Cl<sub>2</sub> at 4 °C. Spectral data for 1: *Anal.* Calc. for C<sub>25</sub>H<sub>11</sub>O<sub>11</sub>Os<sub>3</sub>PS<sub>2</sub>: C, 26.04; H, 0.96. Found: C, 26.38; H, 1.01%. IR ( $v_{co}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2109 m, 2056 s, 2036 m, 2019 s, 1989 m, 1977 m, 1954 w cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.67 (m, 2H), 7.43 (m, 4H), 7.34 (m, 3H), 7.20 (m, 2H). <sup>31</sup>P{1H} NMR (CDCl<sub>3</sub>):  $\delta$  -30.5 (s). MS (m/z): 1152 (M<sup>+</sup>).

## 2.2. Reaction of [Os<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>] with PPhTh<sub>2</sub>

To a CH<sub>2</sub>Cl<sub>2</sub> solution (30 mL) of  $[Os_3(CO)_{10}(NCMe)_2]$  (200 mg, 0.214 mmol) was added PPhTh<sub>2</sub> (121 mg, 0.441 mmol) and the mixture was stirred at 25 °C for 24 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH<sub>2</sub>Cl<sub>2</sub> (7:3, v/v) developed two bands which afforded **1** (45 mg, 18%) and  $[Os_3(CO)_{10}(PPhTh_2)_2]$  (**2**) (190 mg, 63%) as orange crystals after recrystallization from hexane/CH<sub>2</sub>Cl<sub>2</sub> at 4 °C. Spectral data for **2**: *Anal.* Calc. for C<sub>38</sub>H<sub>22</sub>O<sub>10</sub>Os<sub>3</sub>P<sub>2</sub>S<sub>4</sub>: C, 32.61; H, 1.58. Found: C, 32.87; H, 1.64%. IR ( $\nu_{co}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2088 w, 2033 s, 2014 m, 2001 vs 1972 m, 1957 w cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.62 (m, 4H), 7.39 (m, 14H), 7.18 (m, 4H). <sup>31</sup>P{1H} NMR (CDCl<sub>3</sub>): major isomer:  $\delta$  –31.6 (br, s); minor isomer:  $\delta$  –34.8 (br, s). MS (*m*/*z*): 1398 (M<sup>+</sup>).

## 2.3. Thermolysis of 1

An octane solution (15 mL) of **1** (45 mg, 0.039 mmol) was heated to reflux for 5 h. The solvent was removed under reduced pressure. Preparative TLC of the residue on silica gel, using hexane/CH<sub>2</sub>Cl<sub>2</sub> (4:1, v/v) as eluent developed two bands. The second band afforded  $[Os_3(CO)_9{\mu_3-PPhTh(C_4H_2S)}(\mu-H)]$  (**4**) (16 mg, 37%) as yellow crystals from hexane/CH<sub>2</sub>Cl<sub>2</sub> at 4 °C while the first band gave too little product for complete characterization. Spectral data for **4**: *Anal.* Calc. for C<sub>23</sub>H<sub>11</sub>O<sub>9</sub>Os<sub>3</sub>PS<sub>2</sub>: C, 25.18; H, 1.01. Found: C, 25.49; H, 1.05%. IR ( $\nu_{co}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2087 s, 2059 s, 2031 s, 2015 m, 1988 m, 1959 w cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): aromatic region (both isomers):  $\delta$  7.93 (m, 5H), 7.82 (m, 1H), 7.58 (m, 9H), 7.39 (m, 1H), 7.30 (m, 9H), 7.04 (m, 4H), 6.83 (m, 1H); hydride region: major isomer:  $\delta$  –17.89 (d, *J* = 15.2 Hz), minor isomer:  $\delta$  –21.8 (s); minor isomer:  $\delta$  –17.9 (s).

# 2.4. Thermolysis of 2

An octane solution (20 mL) of 2 (75 mg, 0.054 mmol) was heated to reflux for 5 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/ $CH_2Cl_2$  (7:3, v/v) developed two bands. The slower moving band afforded  $[Os_3(CO)_8(PPhTh_2){\mu_3-PPhTh}(C_4H_2S)](\mu-H)]$  (5) (40 mg, 55%) as orange crystals from hexane/CH<sub>2</sub>Cl<sub>2</sub> at 4 °C while the content of the faster moving band was too small for complete characterization. Spectral data for 5: Anal. Calc. for C<sub>37</sub>H<sub>22</sub>O<sub>8</sub>Os<sub>3</sub>P<sub>2</sub>S<sub>4</sub>: C, 32.18; H, 1.65. Found: C, 32.44; H, 1.71%. IR  $(v_{co}, CH_2Cl_2)$ : 2073 s, 2029 s, 2010 s, 1991 m, 1983 m, 1955 m cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): aromatic region (both isomers):  $\delta$  7.85 (m, 2H), 7.64 (m, 2H), 7.50 (m, 3H), 7.43 (m, 1H), 7.28 (m, 1H), 7.14 (m, 4H), 7.01 (m, 1H), 6.95 (m, 2H), 6.78 (m, 2H), 6.46 (m, 2H), 6.24 (m, 1H); hydride region: major isomer:  $\delta$  –17.22 (dd, J = 15.6, 10.8 Hz), major isomer:  $\delta$  –17.42 (dd, J = 15.6, 10.8 Hz). <sup>31</sup>P{1H} NMR (CDCl<sub>3</sub>): major isomer:  $\delta$  –21.5 (s), –17.6 (s); minor isomer:  $\delta - 18.5$  (s), -11.5 (s).

# 2.5. Reaction of [Os<sub>3</sub>(CO)<sub>12</sub>] with PPhTh<sub>2</sub>

PPhTh<sub>2</sub> (121 mg, 0.441 mmol) was added to a toluene solution (30 mL) of  $[Os_3(CO)_{12}]$  (200 mg, 0.221 mmol) and the mixture

was then heated to reflux for 8 h. The solvent was removed by rotary evaporation and the residue subjected to TLC on silica gel for chromatographic separation. Elution with hexane/ $CH_2Cl_2$  (7:3, v/v) developed four bands. The first band gave unreacted  $[Os_3(CO)_{12}]$ (trace). The second band gave a mixture of 1 and 4 (98 mg) while the third band afforded a mixture of 2 and 5 (71 mg). Compounds 1 and 4 had not been separated by chromatographic techniques due to their similar R<sub>f</sub> value while fractional crystallization technique was doubtful in this case since the crystals of both compounds have the same yellow color. The same arguments are true for compound 2 and 5. The fourth band afforded [Os<sub>3</sub>(- $CO_{9}(PPhTh_{2})_{3}$  (3) (17 mg, 5%) as red crystals from hexane/ $CH_{2}Cl_{2}$ at 4 °C. Spectral data for 5: Anal. Calc. for C<sub>51</sub>H<sub>33</sub>O<sub>9</sub>Os<sub>3</sub>P<sub>3</sub>S<sub>6</sub>: C, 37.22; H, 2.02. Found: C, 37.53; H, 2.08%. IR ( $\nu_{CO}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2001 m, 1979 s, 1947 m cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.57 (m, 6H), 7.39 (m, 21H), 7.14 (m, 6H). <sup>31</sup>P{1H} NMR (CDCl<sub>3</sub>):  $\delta$  –33.7 (s). MS (m/z): 1644 (M<sup>+</sup>).

#### 2.6. Thermolysis of 3

An octane solution (15 mL) of **3** (17 mg, 0.010 mmol) was heated to reflux for 45 min. A similar chromatographic separation to that above afforded **5** (5 mg, 36%).

# 2.7. Crystallography

Single crystals of **4** suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution at 4 °C. All geometric and crystallographic data were collected at 150 K on a Bruker SMART APEX CCD diffractometer using Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data reduction and integration was carried out with SAINT+ and absorption corrections were applied using the program SADABS [11]. The structure was solved by direct methods and developed using alternating cycles of least-squares refinement

# Table 1

Crystallographic data and s	structure refinement for 4
-----------------------------	----------------------------

Empirical formula	$C_{23}H_{11}O_9Os_3PS_2$
Formula weight	1097.01
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	10.3403(13)
b (Å)	12.5841(16)
c (Å)	20.625(3)
α (°)	90
β (°)	92.279(2)
γ (°)	90
Volume (Å <sup>3</sup> )	2681.6(6)
Z	4
$D_{\text{calc}}$ (mg/m <sup>3</sup> )	2.717
Absorption coefficient $(mm^{-1})$	14.445
F(000)	1984
Crystal size (mm <sup>3</sup> )	$0.42 \times 0.38 \times 0.22$
$\theta$ Range for data collection (°)	1.90-28.40
Index ranges	$-13 \leq h \geq 13$
	$-16 \leq k \geq 16$
	$-27 \leq l \geq 26$
Reflections collected	22141
Independent reflections	$6382 [R_{int} = 0.0551]$
Completeness to $\theta = 67.10^{\circ}$	99.80%
Refinement method	Full-matrix least-squares on $F^2$
Maximum and minimum transmission	0.1433 and 0.0645
Data/restraints/parameters	6382/0/332
Goodness-of-fit on $F^2$	1.086
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0435, wR_2 = 0.1041$
R indices (all data)	$R_1 = 0.0480, wR_2 = 0.1070$
Largest difference in peak and hole ( $e Å^{-3}$ )	3.833 and -2.689

and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in the calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). The SHELXTL PLUS V6.10 program package was used for structure solution and refinement [12]. Final difference maps did not show any residual electron density of stereochemical significance. The details of the data collection and structure refinement are given in Table 1.

## 3. Results and discussion

# 3.1. Synthesis of simple substitution complexes $[Os_3(CO)_{12-n}(PPhTh_2)_n]$

Treatment of  $[Os_3(CO)_{11}(NCMe)]$  with PPhTh<sub>2</sub> at ambient temperature afforded the mono-phosphine substituted cluster  $[Os_3(-CO)_{11}(PPhTh_2)]$  (1) (87%), while with  $[Os_3(CO)_{10}(NCMe)_2]$  both 1 (18%) and  $[Os_3(CO)_{10}(PPhTh_2)_2]$  (2) (63%) were isolated. Refluxing



Chart 1.



Scheme 1.



**Fig. 1.** Molecular structure of  $[Os_3(CO)_9[\mu_3-PPhTh(C_4H_2S)](\mu-H)]$  (**4**) with thermal ellipsoids drawn at the 50% probability level. Ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os(1)-Os(2) 2.8689(6), Os(1)-Os(3) 3.0171(6), Os(2)-Os(3) 2.7701(5), Os(1)-P(1) 2.344(2), Os(2)-C(10) 2.341(8), Os(3)-C(11) 2.110(9), Os(2)-C(11) 2.343(9), Os(2)-Os(1)-Os(3) 56.082(11), Os(3)-Os(2)-Os(1) 64.667(14), Os(2)-Os(3)-Os(1) 59.251(13), P(1)-Os(1)-Os(2) 73.15(5), P(1)-Os(1)-Os(3) 85.89(5), C(11)-Os(3)-Os(1) 84.8(2), C(10)-Os(2)-Os(1) 77.29(19), C(11)-Os(2) 55.4(2), C(11)-Os(2)-Os(3) 47.8(2), C(11)-Os(2)-Os(1) 84.4(2), C(10)-Os(2)-C(11) 35.4(3), C(1)-Os(3)-Os(1) 114.7(3).

a toluene solution of  $Os_3(CO)_{12}$  and two equivalents of PhPTh<sub>2</sub> gave a complex mixture of five compounds including 1-2 and tris-substituted  $[Os_3(CO)_9(PPhTh_2)_3]$  (3) (5%). All three were easily characterized by spectroscopic methods, the patterns of their IR spectra being very similar to those of phosphine-substituted triosmium clusters [8,9,13-18]. The mass spectra of all three show molecular ions (*m*/*z* 1152 for **1**, *m*/*z* 1398 for **2**, *m*/*z* 1644 for **3**) together with ions due to successive loss of all carbonyls, while <sup>1</sup>H NMR spectra showed only aromatic resonances indicating that metalation had not taken place. The <sup>31</sup>P{1H} NMR spectrum of **1** and **3** both consist only of a singlet, the latter showing that all three phosphines occupy equivalent sites. In contrast the room temperature <sup>31</sup>P{1H} NMR spectrum of **2** displays two broad singlets in 3:1 intensity ratio. This is consistent with existence of an interconverting mixture of transtrans and cis-trans isomers (cis or trans with respect to the Os-Os vector, Chart 1) [8.9.16.17]. Nordlander and co-workers have previously noted a similar mixture of isomers for  $[Os_3(CO)_{10}(PPh_2Th)_2]$ their interconversion being slow on the NMR timescale at -60 °C and have crystallographically characterized the *cis-trans* isomer. A similar conversion of isomers clearly occurs in 2 [8].

## 3.2. Carbon-hydrogen bond activation of a coordinated PPhTh<sub>2</sub> ligand

Heating **1** and **2** in refluxing octane affords  $[Os_3(CO)_9$ { $\mu_3$ -PPhTh(C<sub>4</sub>H<sub>2</sub>S)}( $\mu$ -H)] (**4**) (37%) and  $[Os_3(CO)_8(PhPTh_2)$ { $\mu_3$ -PPhTh(C<sub>4</sub>H<sub>2</sub>S)}( $\mu$ -H)] (**5**) (55%), respectively (Scheme 1) both resulting from activation of a carbon–hydrogen bond of a coordinated PPhTh<sub>2</sub> ligand. Likewise, heating **3** under similar conditions gave **5** (36%).

The precise nature of this process was confirmed *via* a single crystal X-ray diffraction (Fig. 1) of 4. The molecule contains a triangular core of osmium atoms with three distinctly different metalmetal bonds [Os(1)-Os(2) 2.8689(6), Os(1)-Os(3) 3.0171(6) and Os(2)–Os(3) 2.7701(5) Å] ligated by nine carbonyls, a  $\mu_3$ -PPhTh( $C_4H_2S$ ) ligand and a bridging hydride. The  $\mu_3$ -PPhTh( $C_4H_2S$ ) ligand is axially coordinated to Os(1) through the phosphorus atom, to Os(3) through a Os–C  $\sigma$ -bond [Os(3)–C(11) 2.110(9)Å] and to Os(2) through an  $\eta^2$  ( $\pi$ )-interaction between C(10), C(11) and Os(2) [Os(2)-C(10) 2.341(8) and Os(2)-C(11) 2.343(9) Å], thus producing a  $\sigma$ , $\pi$ -vinyl type bridge between Os(2) and Os(3). As a result the thienyl ring is tilted towards Os(2). This type of coordination mode of the thienyl moiety is also observed in the related clusters  $[Ru_3(CO)_9[\mu_3-PPh_2(C_4H_2S)](\mu-H)]$  [6],  $[Os_3(CO)_9[\mu_3-PPh_2(C_4H_2S)](\mu-H)]$  [6],  $[Os_3(CO)_9[\mu_3-PPh_2(C_4H_2S)](\mu-H)]$  $PPh_2(C_4H_2S)(\mu-H)$  [8] and  $[Os_3(CO)_9(\mu_3-PTh_2(C_4H_2S))(\mu-H)]$  [9]. The hydride ligand is not located in the structural analysis, but from the lengthening of the Os(1)-Os(3) edge compared to the other two edges of the cluster (vide supra) and spread out of the Os-Os-CO angles along this edge [C(1)-Os(1)-Os(3) 115.3(3)], C(9)-Os(3)-Os(1) 114.7(3)°] we speculate that the hydride span across this Os(1)–Os(3) edge. This assumption is also akin to the observation that the hydride bridges the metalated edge in related clusters [6,8,9]. We also undertook a solid-state investigation of compound 5, and partially determined its molecular structure [19]. The refinement of this structure is poor due to severe disorder associated with the phenyl and thienyl rings which precludes discussion of the structural details. However, the structure gives sufficient information about the geometry of the cluster and the orientation of the ligands on the cluster surface. Cluster 5 differs from **4** only in the substitution of a carbonyl by a PPhTh<sub>2</sub> ligand, which occupies an equatorial coordination site on Os(2).

In solution both **4** and **5** exist in two isomeric forms. Thus, the <sup>31</sup>P{1H} NMR spectrum of **4** displays two singlets at  $\delta$  –21.8 and –17.9 (relative intensity 2.5:1), while **5** shows four singlets at  $\delta$  –21.5, –18.5, –17.6 and –11.5 in 7:1:7:1 intensity ratio. Consistent with this, the hydride region of the <sup>1</sup>H NMR spectra display



two doublets at  $\delta$  –17.89 and –18.20 (*J* = 15.2 Hz) for **4**, while two doublets of doublets at  $\delta$  –17.22 and –17.42 (*J* = 15.6, 10.8 Hz) are seen for **5**. This isomerism is almost certainly a result of the different orientations of the phenyl and thienyl groups with respect to the osmium triangle. Thus in the crystal structure of **4** the phenyl group is orientated on the same side of the molecule as the metalated thienyl ligand (**4a**), while a second orientation is also possible (**4b**) (Chart 2). On the basis on the NMR data discussed above we cannot discern which isomer is which and simply suggest that it is likely that the most abundant isomer in solution is that seen in the X-ray structure. Similar isomers are also observed for **5** and the disorder noted in the X-ray structure is presumably a result of the co-crystallization of these.

# Acknowledgement

Financial support of this work by the University Grants Commission of Bangladesh is gratefully acknowledged.

#### **Appendix A. Supplementary material**

CCDC 753392 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via 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.ica.2010.01.030.

#### References

- A.J. Deeming, M.K. Shinhmar, A.J. Arce, Y.De. Sanctis, J. Chem. Soc., Dalton Trans. (1999) 1153.
- [2] M.N. Uddin, M.A. Mottalib, N. Begum, S. Ghosh, A.K. Raha, D.T. Haworth, S.V. Lindeman, T.A. Siddiquee, D.W. Bennett, G. Hogarth, E. Nordlander, S.E. Kabir, Organometallics 28 (2009) 1514.
- [3] S.P. Tunik, I.G. Koshevoy, A.J. Poë, D.H. Farrar, E. Nordlander, M. Haukka, P.A. Pakkanen, J. Chem. Soc., Dalton Trans. (2003) 2457.
- [4] J.D. King, M. Monari, E. Nordlander, J. Organomet. Chem. 573 (1999) 272.
- [5] U. Bodensieck, H. Varenkamp, G. Rheinwald, H. Stoeckli-Evans, J. Organomet. Chem. 488 (1995) 85.
- [6] A.J. Deeming, S.N. Jaysuriya, A.J. Arce, Y.De. Sanctis, Organometallics 15 (1996) 786.
- [7] M.N. Uddin, N. Begum, M.R. Hassan, G. Hogarth, S.E. Kabir, M.A. Miah, E. Nordlander, D.A. Tocher, J. Chem. Soc., Dalton Trans. (2008) 6219.
- [8] N.K. Kiriakidou Kazemifar, M.J. Stchedroff, M.A. Mottalib, S. Selva, M. Monari, E. Nordlander, Eur. J. Inorg. Chem. (2006) 2058.
- [9] M.A. Mottalib, S.E. Kabir, D.A. Tocher, A.J. Deeming, E. Nordlander, J. Organomet. Chem. 692 (2007) 5007.
- [10] B.F.G. Johnson, J. Lewis, D.A. Pippard, J. Chem. Soc., Dalton Trans. (1981) 407.
- [11] SMART and SAINT Software for CCD diffractometers, version 6.1, Madison, WI, 2000.
- [12] G.M. Sheldrick, SHELXTL PLUS, version 6.1, Bruker AXS, Madison, W1, 2000.
- [13] M.I. Bruce, B.K. Nicholson, M.L. Williams, J. Organomet. Chem. 243 (1983) 69.
  - [14] M.I. Bruce, J.G. Matisons, B.K. Nicholson, J. Organomet. Chem. 247 (1983) 321.
  - [15] M.I. Bruce, M.L. Williams, B.K. Nicholson, J. Organomet. Chem. 258 (1983) 63.
  - [16] R.F. Alex, R.K. Pomeroy, Organometallics 6 (1987) 2437.
  - [17] A.J. Deeming, S. Donovan-Mtunzi, S.E. Kabir, P.J. Maning, J. Chem. Soc., Dalton Trans. (1985) 1037.
  - [18] M.I. Bruce, M.J. liddell, C.A. Hughes, J.M. Patrick, B.W. Skelton, A.H. White, J. Organomet. Chem. 347 (1988) 181.
  - [19] Crystallographic data of **5**: space group  $P2_12_12_1$ , with a = 12.5603 Å, b = 15.0321 Å, c = 20.1179 Å,  $\alpha = 90^{\circ}$ ,  $\beta = 90^{\circ}$ ,  $\gamma = 90^{\circ}$ , Os(1)-Os(2) 2.7775, Os(1)-Os(3) 2.8592, Os(2)-Os(3) 3.0182, Os(2)-P(2) 2.3204, Os(3)-P(1) 2.3476 Å.