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Insertion of Pt into C–H and C–S bonds of thiophene derivatives. The X-ray crystal structure of a thiaplatinacycle of 3,6-dimethylthieno[3,2-*b*]thiophene

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Abstract

Treatment of the zerovalent platinum complex $[Pt(PEt_3)_4]$ with 3,6-dimethylthieno[3,2-*b*]thiophene leads to a six-membered, approximately planar thiaplatinacycle, which has been characterised spectroscopically and by a single crystal X-ray determination. The reaction of $[Pt(PEt_3)_4]$ with 2,2′-bithiophene and 1-methyl-2-(2-thienyl)pyrrole produced two types of products, thiaplatinacycles resulting from C–S insertion and platinum(II) hydrides arising from C–H insertion. These complexes were characterised spectroscopically.

Keywords: Platinum hydrides; Oxidation; C–H activation; C–S activation; Thiaplatinacycles; Crystal structure

1. Introduction

Hydrodesulfurisation (HDS) is an important industrial process by which sulfur is removed from petroleum feedstocks by treatment with hydrogen gas over heterogeneous catalysts. Despite the importance of HDS in reducing noxious emissions, the mechanism of HDS is not fully understood. Studies have been undertaken in order to study C–S bond scission in homogeneous solution by organometallic complexes in order to gain some insights into the possible reaction intermediates and nature of kinetics on heterogeneous catalysts. C–S bond activation is also of interest in studies of catalytic and stoichiometric transformations of organic sulfides [1]. For example, the Pd(0) and Pt(0) catalysed carbothiolation of alkynes involves the oxidative addition of the metal (M) into a C–S bond, insertion of an alkyne into the S–M bond and subsequent reductive elimination [2].

Various metallacycles [3–5] have been prepared in which a metal fragment (e.g. Rh, Ir, Pt, Fe, W) oxidatively inserts into the C–S bonds of thiophenes, benzothiophenes and dibenzothiophenes [6–13]. Thiairidacycles [13] and thiaplatinacycles [10,14] have both been shown to effect HDS. This article reports on the oxidative reactions of platinum(0) with the thiophene derivatives 3,6-dimethylthieno[3,2-*b*]thiophene (**1**), 2,2′-bithiophene (**2**) and 1-methyl-2-(2-thienyl)pyrrole (**3**) (Scheme 1). In addition to the expected C–S insertion products, the competitive process of C–H activation was also found to occur to generate platinum(II) hydrides.

2. Experimental

2.1. General

All manipulations involving metal complexes were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen [15], unless stated otherwise. Solvents were distilled under nitrogen from appropriate drying agents before use. The $[Pt(PEt_3)_4]$ precursor was

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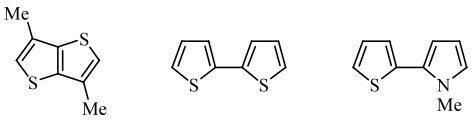


1 2 3

Scheme 1.

prepared from $K_2[PtCl_4]$ according to a literature method [16]. 1-Methylpyrrole and *N*,*N*,*N*′*N*′-tetramethylethylenediamine (tmeda) were freshly distilled prior to use. The dppf (where dppf = 1,1′-bis(diphenylphosphanyl)ferrocene) and [$PdCl_2$dppf] catalyst were prepared as previously reported [17]. All other reagents and chemicals were obtained commercially and used as received. The ^{1}H-, ^{31}P{^{1}H}- and ^{13}C{^{1}H}-NMR spectra were recorded on a Bruker ARX300 spectrometer operating at 300.133, 121.496 and 75.469 MHz for the respective nuclei. Chemical shifts in ^{1}H- and ^{13}C{^{1}H}-NMR spectra were calibrated with reference to residual proton signals of the deuterated solvent (7.24 and 77.0 ppm respectively for $CDCl_3$). ^{31}P{^{1}H}-NMR spectra were referenced to the deuterated lock signal, which had previously been referenced to 85% H_3PO_4. Electron impact (EI) mass spectra were recorded on a Finnigan Mat 8200 instrument operating at 70 eV and fast atom bombardment (FAB) mass spectra were measured on a VG 7070-E instrument (Xe beam).

2.2. Crystal structure determination

The intensity data for compound **4** was collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo–K_α radiation. Data were corrected for Lorentz and polarisation effects, and for absorption effects [18,19]. The structure was solved by direct methods (SHELXS [20]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [21]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [21]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

2.2.1. Crystal data for **4** (see Section 5)

$C_{20}H_{38}P_2PtS_2$, Mr = 599.65 g mol^{-1}, gold–yellow prism, size 0.12 × 0.12 × 0.12 mm^3, orthorhombic, space group $P2_12_12_1$, a = 9.8621(4), b = 13.3149(6), c = 18.6497(8) Å, $\alpha = \beta = \gamma = 90.00°$, V = 2448.9(2) Å^3, T = −90 °C, Z = 4, ρ_{calcd} = 1.626 g cm^{-3}, μ(Mo–K_α) = 60.33 cm^{-1}, psi-scan, transmin: 0.4098, transmax: 0.5313, $F(000)$ = 1192, 13 153 reflections in $h(-12/12)$, $k(-15/17)$, $l(-24/20)$, measured in the range $3.01 \leq \Theta \leq 27.41°$, completeness Θ_{max} = 99.4%, 5516 independent reflections, R_{int} = 0.078, 4400 reflections with $F_o > 4\sigma(F_o)$, 226 parameters, 0 restraints, $R1_{obs}$ = 0.080, wR^2_{obs} = 0.088, $R1_{all}$ = 0.114, wR^2_{all} = 0.094, GOOF = 1.062, Flack-parameter −0.01(1), largest difference peak and hole: 3.862/−1.958 e Å^{-3}.

2.3. Preparation of the thiophenic substrates

2.3.1. Preparation of 3,6-dimethylthieno[3,2-*b*]thiophene (**1**)

The ligand was prepared in a manner similar to that described by Choi and co-workers [22]. A mixture of 2,5-dihydroxy-2,5-dimethyl-3-hexyne (17.0 g, 120 mmol) and elemental sulfur (9.52 g, 297 mmol) and benzene (130 ml) was sealed in an autoclave and heated overnight at 200 °C. After cooling to room temperature (r.t.), the autoclave was opened and the brown residue obtained was extracted with benzene. The solvent was removed in vacuo and the resulting residue was dissolved in warm hexane and filtered. Purification by column chromatography on silica gel with hexane as the eluent resulted in the isolation of a white solid, **1**. Yield 3.55 g (21%). ^{1}H-NMR δ ($CDCl_3$): 6.949 (α-*H*, 2H, s), 2.354 (C*H*$_3$, 6H, d, $^4J_{HH}$ = 0.8 Hz). ^{13}C-NMR δ ($CDCl_3$): 140.08 (*ipso-C*), 130.37 (*ipso-C*), 121.80 (*C*H), 14.63 (*C*H$_3$).

2.3.2. Preparation of 1-methyl-2-(2-thienyl)pyrrole (**3**)

Under an argon atmosphere, 1-methylpyrrole (4.02 g, 49.6 mmol) was slowly added to a Schlenk flask containing a 1.6 M *n*-BuLi/hexane solution (38 ml, 60 mmol) and tmeda (8.30 ml, 55 mmol) in hexane (60 ml) [23]. The solution was heated under reflux for 20 min. After allowing the solution to cool to r.t., THF (40 ml) was added. The solution was vigorously stirred as anhydrous $ZnCl_2$ (9.0 g, 66 mmol) was added. The temperature of the mixture was controlled by an external bath so that the temperature did not rise above 20 °C. 2-Bromothiophene (4.8 ml, 50 mmol) and [$PdCl_2$dppf] catalyst (0.54 g, 0.74 mmol) were added and the reaction mixture was heated to reflux for 6 h. After cooling to r.t. the solution was poured onto a 2.8 M NH_4Cl (aq) solution to which a small amount of NH_3 had been added. The organic layer was separated and the aqueous phase was treated with Et_2O (4 × 100 ml). The organic fractions were combined and dried over anhydrous K_2CO_3. The solvent was removed under reduced pressure and the product isolated by distillation (b.p. 125 °C/15 mmHg). Yield 5.51 g (68%) slightly brown oil stored under Ar. ^{1}H-NMR δ ($CDCl_3$): 7.244 (C$H_{thienyl}$, 1H, dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.3 Hz), 7.051 (C$H_{thienyl}$, 1H, m), 7.010 (C$H_{thienyl,}$ 1H, dd, $^3J_{HH}$ = 3.6 Hz, $^4J_{HH}$ = 1.3 Hz), 6.687 (C$H_{pyrrole}$, 1H, t, $^3J_{HH}$ = 2.3 Hz), 6.316 (C$H_{pyrrole}$, 1H, dd, $^3J_{HH}$ = 3.6 Hz, $^4J_{HH}$ = 1.8 Hz), 6.512 (C$H_{pyrrole}$, 1H, dd, $^3J_{HH}$ = 3.6 Hz, $^4J_{HH}$ = 2.8 Hz), 3.703 (CH_3, 3H, s) ppm.

2.4. Preparation of platinum(II) compounds

2.4.1. Reaction of [Pt(PEt$_3$)$_4$] with 3,6-dimethylthieno[3,2-b]thiophene (4)

Under an Ar atmosphere, [Pt(PEt$_3$)$_4$] (0.55 g, 0.82 mmol) was weighed into a clean, dry Schlenk flask and dissolved in toluene (5 ml). Solid 3,6-dimethylthieno[3,2-*b*]thiophene (0.278 g, 1.65 mmol) and 10 ml of toluene were added. The mixture was heated to 80 °C under high vacuum for 6 h and then refluxed for 3 h. Thereafter the heat source was removed and the mixture stirred overnight at r.t. to form an off-white solid precipitate. The supernatant was removed and the precipitate washed with hexane (2 × 1 ml) and dried in vacuo. Ivory-coloured crystals suitable for X-ray crystallography studies were obtained from a saturated toluene/hexane solution of **4** at −20 °C. Yield 0.33 g (67%) $C_{20}H_{38}P_2PtS_2$: Calc.: C, 40.06; H, 6.39. Found: C, 39.90; H, 6.42%. ^{1}H-NMR δ ($CDCl_3$): 7.278 (C*H*, 1H, dd, $^3J_{P,H} = 7.8$ Hz, $^3J_{P,H} = 25.6$ Hz, $^4J_{H,H}$ and $^2J_{Pt,H}$ unresolved), 6.785 (C*H*, 1H, s, long-range $J_{Pt,H} = 9.8$ Hz, $^4J_{H,H}$ unresolved), 2.462 (CH_3, 3H, d, $^4J_{H,H} = 0.8$ Hz), 2.369 (CH_3, 3H, d, $^4J_{H,H} = 1.0$ Hz), 2.00 (PCH_2, 12H, m), 1.12 (PCH_2CH_3, 18H, m) ppm. ^{13}C{^{1}H}-NMR δ ($CDCl_3$): 139.04 (*ipso*-*C*, d, $^3J_{P,C} = 7.2$ Hz), 137.70 (*ipso*-*C*), 137.57 (*ipso*-*C*), 131.86 (*C*H, dd, $^2J_{P,cis\text{-}C} = 9.4$ Hz, $^2J_{P,trans\text{-}C} = 100.1$ Hz, $^1J_{Pt,C}$ not observed), 128.80 (*ipso*-*C*), 116.24 (*C*H), 28.44 (*C*H$_3$, d, $^4J_{P,C} = 11.7$ Hz, $^3J_{Pt,C} = 59.2$ Hz), 16.56 (*C*H$_3$), 16.6 (P*C*H$_2$, m), 8.4 (PCH_2CH_3, m) ppm. ^{31}P{^{1}H}-NMR δ ($CDCl_3$): 11.98 (*P trans* to S, d, $^2J_{P,P} = 22.9$ Hz, $^1J_{Pt,P} = 3140$ Hz), 0.20 (*P trans* to C, d, $^2J_{P,P} = 22.9$ Hz, $^1J_{Pt,P} = 1696$ Hz) ppm. EIMS (70 eV): *m*/*z* 599 [M$^+$, 48%], 431 [M$^+$ − $S_2C_8H_8$, 76%], 402 [M$^+$ − $S_2C_8H_8$ − Et, 76%], 373 [M$^+$ − $S_2C_8H_8$ − 2Et, 87%], 168 ($S_2C_8H_8^+$, 100%), 118 (PEt_3^+, 34%).

2.4.2. Reaction of [Pt(PEt$_3$)$_4$] with 2,2′-bithiophene (**5a** and **5b**)

Solid 2,2′-bithiophene (0.42 g 2.5 mmol) was added to a Schlenk flask containing [Pt(PEt$_3$)$_4$] (1.87 g, 2.8 mmol) in toluene (20 ml). The mixture was stirred for 5 h at 80 °C and then at r.t. overnight. The solvent was removed in vacuo to yield a brown oil containing a mixture of **5a** and **5b** (4:1 as determined by NMR). EIMS (70 eV): *m*/*z* 597 [M$^+$, 2%], 431 [M$^+$ − $S_2C_8H_6$, 2%], 402 [M$^+$ − $S_2C_8H_6$ − Et, 3%], 373 [M$^+$ − $S_2C_8H_6$ − 2Et, 3%], 166 ($S_2C_8H_6^+$, 100%).

2.4.3. Reaction of [Pt(PEt$_3$)$_4$] with 1-methyl-2-(2-thienyl)pyrrole (**6a** and **6b**)

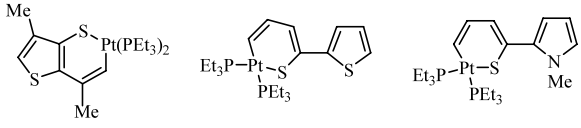
To a solution of [Pt(PEt$_3$)$_4$] (2.26 mmol) in 10 ml toluene was added 1-methyl-2-(2-thienyl)pyrrole (0.56g, 3.4 mmol). The reaction mixture was stirred under reflux for 48 h. A mixture of **6a** and **6b** (1:1.3 as determined by NMR) was obtained after removal of the solvent in vacuo. FABMS: *m*/*z* 594 [M$^+$, 17%], 537 [M$^+$ − Et − C_2H_4, 18%], 476 [M$^+$ − PEt_3, 5%], 431 [M$^+$ − C_9H_9NS, 30%], 402 ($Pt\{PEt_3\}_2^+$ − Et, 19%), 375 ($Pt\{PEt_3\}_2^+$ − 2 C_2H_4, 16%), 347 ($Pt\{PEt_3\}_2^+$ − 3 C_2H_4, 10%), 164 ($C_9H_9NSH^+$, 11%), 163 ($C_9H_9NS^+$, 11%), 135 ($HOPEt_3^+$, 100%), 119 ($HPEt_3^+$, 20%). Accurate mass: 594.1926 (calculated), 594.1928 (observed).

3. Results and discussion

When a twofold excess of 3,6-dimethylthieno[3,2-*b*]thiophen (**1**) was refluxed with tetrakis(triethylphosphane) platinum(0) in toluene for 3 h, a thiaplatinacycle complex, **4**, was obtained (Scheme 2). The complex was characterised by NMR and mass spectrometry and the structure was confirmed by a single crystal X-ray diffraction study.

Ivory-coloured crystals suitable for single crystal X-ray diffraction studies were grown from a cold, saturated solution of **4** in toluene/hexane. Complex **4** has an orthorhombic crystal system and crystallised in the space group $P2_12_12_1$. The six-membered thiaplatinacycle is close to planar, while the five-membered thiophene ring is planar (Table 1). A molecular representation of **4** is given in Fig. 1.

The platinum atom is in a near square planar coordination geometry. The bond angle P(1)–Pt–P(2) of 97.73(9)° is considerably larger than the ideal square planar value of 90° (Table 2), probably to allow room for the free rotation of the phosphane ethyl substituents [10]. Insertion of the Pt-centre into the C(1)–S(1) bond causes the internal angle at S(1) to increase relative to the angle at S(2), i.e. C(6)–S(1)–Pt 112.0(4)° versus C(3)–S(2)–C(4) 90.8(6)°. The remaining bond angles of the thiaplatinacycle are all larger than the 120° expected for a delocalised six-membered ring system such as benzene or thiabenzene or thiaplatinabenzene. The C–C bond lengths in the thiaplatinacycle, show that the ring is a non-conjugated system, where C(1)–C(2) is a localised double bond, C(2)–C(3) a single bond and C(3)–C(6) represents a bond order of between one and two (Table 3). The Pt–P bond lengths illustrate the difference in the *trans* influence of the S- and C-bound atoms; the C-atom having a greater *trans* influence than the S-atom. The bond lengths and bond angles about the platinum centre in **4** correspond quite well with thiaplatinacycles of benzothiophene [10], 3-methylthiophene



4 **5a** **6a**

Scheme 2.

Table 1
Selected torsion angles (°) of **4**

C(1)–Pt–S(1)–C(6)	−13.8(5)	C(4)–S(2)–C(3)–C(6)	−0.5(8)
S(1)–Pt–C(1)–C(2)	−9.2(11)	C(3)–S(2)–C(4)–C(5)	1.6(10)
C(1)–C(2)–C(3)–C(6)	−13.5(18)	S(2)–C(4)–C(5)–C(6)	−2.1(14)
S(1)–C(6)–C(3)–C(2)	3.3(17)	S(2)–C(3)–C(6)–C(5)	−0.6(12)
Pt–S(1)–C(6)–C(3)	12.0(10)		

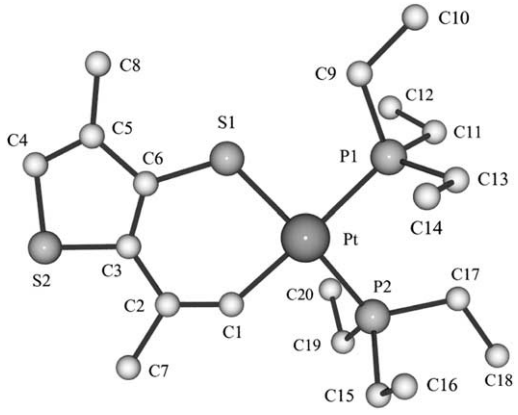


Fig. 1. Ball-and-stick diagram of the molecular structure of **4**.

Table 2
Selected bond angles (°) of **4**

C(1)–Pt–P(2)	85.4(4)	C(3)–S(2)–C(4)	90.8(6)
C(1)–Pt–S(1)	89.8(4)	C(6)–C(3)–S(2)	110.(1)
P(2)–Pt–S(1)	173.7(1)	C(4)–C(5)–C(6)	111.(1)
C(1)–Pt–P(1)	176.1(3)	C(3)–C(6)–C(5)	115.(1)
P(2)–Pt–P(1)	97.73(9)	C(5)–C(4)–S(2)	114.(1)
S(1)–Pt–P(1)	87.24(9)	C(1)–C(2)–C(7)	122.(1)
C(6)–S(1)–Pt	112.0(4)	C(3)–C(2)–C(7)	115.(1)
C(2)–C(1)–Pt	138.(1)	C(2)–C(3)–S(2)	121.(1)
C(1)–C(2)–C(3)	123.(1)	C(5)–C(6)–S(1)	119.(1)
C(3)–C(6)–S(1)	125.8(9)	C(4)–C(5)–C(8)	125.(1)
C(6)–C(3)–C(2)	129.4(9)	C(6)–C(5)–C(8)	124.(1)

[24], 3-methylbenzothiophene [25], as well as 2-nitro- and 3-chlorothiophene [14], reported in the literature.

The insertion reaction is stereoselective and the vinyl C–S bond rather than the aryl C–S bond is the site of attack [10,26]. Furthermore, the thienothiophene molecule, **1**, contains two thiophene moieties which allows for the possibility of a double oxidative insertion to form a unique dithiaplatinacycle. Attempts at preparing such a binuclear complex were unsuccessful despite prolonged heating of the thiaplatinacycle **4** with excess $[Pt(PEt_3)_4]$. The formation of a thiaplatinacycle is known to be reversible [10] and the thiaplatinacycle, the free ligand, dissociated phosphane molecules and the platinum(0) precursor exist in equilibrium.

The ^{31}P-NMR spectrum of **4** displayed two doublets, with accompanying ^{195}Pt satellites, at 11.98 ppm (P *trans* to S) and 0.20 ppm (P *trans* to C). The two non-equivalent phosphorus atoms are coupled by a two bond coupling of 22.9 Hz, a value typical of *cis*-phosphanes [27]. The respective $^1J_{Pt,P}$ couplings of 3139 Hz (P *trans* to S) and 1696 Hz (P *trans* to C) illustrate the large difference in the *trans* influence of the S- and C-bound groups.

Unlike $[Pt(PEt_3)_4]$, the less nucleophilic $[Pt(PPh_3)_3]$ complex does not react with 3,6-dimethylthieno[3,2-*b*]thiophene despite prolonged refluxing in toluene. Instead, thermal degradation of the zerovalent metal phosphane complex leads to the formation of dinuclear species such as $[Pt_2(\mu\text{-}PPh_2)\text{-}\{\mu\text{-}C_6H_4(PPh_2)\text{-}2\}(PPh_3)_2]$ [28].

In contrast to the reaction of $[Pt(PEt_3)_4]$ with the thienothiophene to give **4**, the reactions of $[Pt(PEt_3)_4]$ with 2,2′-bithiophene (**2**) and 1-methyl-2-(2-thienyl)pyrrole (**3**) led to the formation of two types of products. C–S activation gave thiaplatinacycles **5a** and **6a** (Scheme 2). The ^{31}P NMR spectra of these complexes were very similar to that obtained for **4** (Table 4).

The second type of insertion product observed was hydrido platinum(II) complexes, obtained via C–H activation. Oxidative insertion at an unsubstituted α-position of the thienyl rings in 2,2′-bithiophene (**2**) and in 1-methyl-2-(2-thienyl)pyrrole (**3**) led to the formation of **5b** and **6b** respectively (Scheme 3). The separation of complexes **5a/5b** and **6a/6b** by column chromatography led to decomposition. The assignments of the ^{1}H-NMR resonances for **5a/5b** and **6a/6b** (Table 5) were aided by two-dimensional (^{1}H, ^{1}H) homonuclear chemical shift correlation (COSY) experiments.

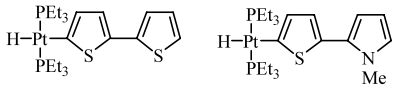
The high field region of the ^{1}H-NMR spectrum of **5b** showed a 1:2:1 triplet resonance at −7.30 ppm with coupling to two equivalent phosphorus atoms ($^2J_{P,H}$ = 17.4 Hz) as well as coupling to platinum-195 ($^1J_{Pt,H}$ = 713 Hz). This data is typical of hydride proton resonances for *trans* H–Pt–C(heteroaryl) type complexes [29,30]. The hydride complex decomposes in

Table 3
Selected bond lengths (Å) of **4**

Pt–C(1)	2.04(1)	S(1)–C(6)	1.75(1)	C(1)–C(2)	1.29(2)
Pt–P(2)	2.279(3)	S(2)–C(3)	1.74(1)	C(2)–C(3)	1.42(2)
Pt–S(1)	2.290(2)	S(2)–C(4)	1.73(2)	C(3)–C(6)	1.37(2)
Pt–P(1)	2.342(2)			C(4)–C(5)	1.33(2)
				C(5)–C(6)	1.43(2)

Table 4
^{31}P-NMR data for thiaplatinacycles **4**, **5a** and **6a**

	4		**5a**		**6a**	
	P *trans* to S	P *trans* to C	P *trans* to S	P *trans* to C	P *trans* to S	P *trans* to C
δ (ppm)	11.98	0.20	11.36	0.50	10.32	0.93
$^1J_{Pt,P}$ (Hz)	3140	1696	3145	1676	3094	1671
$^2J_{P,P}$ (Hz)	22.9	22.9	22.9	22.9	23.4	23.4



5b **6b**

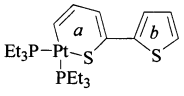
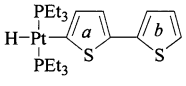
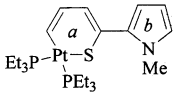
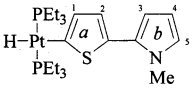
Scheme 3.

deuterated chloroform, presumable due to trace amounts of hydrogen chloride in the solvent. With time the ^{1}H-NMR hydride resonance disappears and a new ^{31}P-NMR singlet resonance at 3.54 ppm ($^1J_{Pt,P}$ = 3470 Hz) takes the place of the original singlet at 18.66 ppm ($^1J_{Pt,P}$ = 2674 Hz). This new resonance is typical of *cis*-[$PtX_2(PEt_3)_2$] complexes, where X = carbon-donor anionic ligand [31]. Similarly, the hydride proton of **6b** gives rise to a triplet pattern at −7.24 ppm ($^2J_{P,H}$ = 17.5 Hz and $^1J_{Pt,H}$ = 713 Hz) in the ^{1}H-NMR spectrum and a singlet at 18.71 ppm ($^1J_{Pt,P}$ = 2680 Hz) in the ^{31}P-NMR spectrum.

The $^{13}C\{^1H\}$-NMR resonances could not be unambiguously assigned due to overlapping of signals and the *ipso*-carbon atoms were obscured by low intensity resonances from decomposition of the platinum(II) complexes in solution.

In general the α-position of heteraromatic rings are more susceptible to derivatisation than the β-position [32]. A diplatinum complex of 2,2′-bithiophene, viz. *trans*, *trans*-[$Cl(PBu_3)_2Pt(\mu$-2,5′-$C_4H_2SC_4H_2S)Pt(PBu_3)_2Cl$] has been reported in the literature, however

Table 5
^{1}H-NMR for **5a**, **5b** and **6a**, **6b**

5a	**5b**	**6a**	**6b**
			
	δ / ppm, with *J* in Hz		
7.39 (d, H_b)	7.51 (m, H_a)	7.21 (dd, H_a)	6.98 (m, H_a2)
$J_{H,H}$ 3.27		$^3J_{H,H}$ 5.2 , $^4J_{H,H}$ 1.0	
7.18 (m, H_a)	7.42 (m, H_b)	7.03 (m, H_a)	6.73 (m, H_a1)
7.11 (m, H_a)	7.13 (m, H_a)	6.59 (m, H_a)	6.66 (m, H_b3)
7.08 (m, H_b)	7.08 (m, H_b)	6.55 (m, H_b)	6.27 (dd, H_b5)
			$^3J_{H,H}$ 3.2 , $^4J_{H,H}$ 1.9
6.92 (m, H_b)	6.97 (m, H_b)	6.18 (m, H_b)	6.11 (m, H_b4)
6.55 (s br, H_a)		6.05 (m, H_b)	
$J_{Pt,H}$ 27.4			
		3.67 (s, Me)	3.71 (s, Me)
1.96 (m, CH_2)	1.68 (m, CH_2)	1.92 (m, CH_2)	1.67 (m, CH_2)
1.17 (m, CH_3)	1.10 (m, CH_3)	1.10 (m, CH_3)	1.05 (m, CH_3)
	-7.30 (t, PtH)		-7.24 (t, PtH)
	$^2J_{P,H}$ 17.4 , $^1J_{Pt,H}$ 713		$^2J_{P,H}$ 17.5 , $^1J_{Pt,H}$ 713

no ^{31}P-NMR data was provided [33]. The related diplatinum thienyl derivative *trans*, *trans*-[Cl(PBu_3)$_2$Pt(μ-2,5-C_4H_2SPt(PBu_3)$_2$Cl] has a ^{31}P-NMR chemical shift of 18.91 ppm with $^1J_{Pt,P}$ of 2673 Hz, which corresponds well with the *trans* diphosphane structure of **5b** and **6b**. The values of the $^1J_{Pt,P}$ coupling constant is characteristic of a *trans*-phosphane platinum(II) hydrido species [29,30].

Studies of the reaction of 1-methylpyrrole with [Pt(PEt_3)$_4$] shows that C–H activation on the pyrrole ring is extremely sluggish [30], and the most likely position of attack of Pt(0) on **3** is at the α-carbon of the thienyl ring. Insertion thus occurs at a C–H bond on the thienyl ring rather than on the pyrrolyl ring, and this is also supported by the ^{1}H-NMR data. Interestingly, insertion of the platinum centre at the C(2)–C(2′) bond which links the thienyl ring to the pyrrolyl ring did not occur. Although C–H activation is generally easier to achieve than C–C oxidative insertion [34], this bond has been found to be readily labilised when attempting to obtain chromium, molybdenum and tungsten carbene derivatives of 1-methyl-2-(2-thienyl)pyrrole [35]. Upon lithiation of the molecule with two to three equivalents of *n*-butyllithium, C(2)–C(2′) bond scission leads to the formation of two separate carbene complexes, namely 2-butylthienyl and 1-methylpyrrolyl derivatives.

When a mixture of two equivalents of 2,2′-bithiophene and one equivalent of [Pt(PEt_3)$_4$] was heated for 20 h in refluxing toluene, a mixture of approximately 1:1.3 (based on NMR data) of **5a** and **5b** was obtained. Increasing the reaction time to 72 h favoured the formation of the thiaplatinacycle **5a** over the hydride **5b**. This was consistent with the conclusion that the C–S insertion product is thermodynamically more stable [36].

Jones and co-workers [37] have shown that both C–H and C–S insertion occurs when [(C_5Me_5)Rh(PMe_3)($H)_2$] is irradiated at low temperature in the presence of thiophene. On warming to r.t., the C–H insertion product [(C_5Me_5)Rh(PMe_3)(2-thienyl)H] isomerised to the thermodynamically more stable C–S insertion product [(C_5Me_5)(PMe_3)Rh(*C*,*S*-C_4H_4S]. Similarly, photochemical reactions of [Fe(dmpe)$_2$($H)_2$] (where dmpe = $Me_2PCH_2CH_2PMe_2$) [11], [C_5H_5)$_2$M($H)_2$] (where M = Mo, W) [6] and *trans*-[Rh(PMe_3)$_2$(CO)Cl] [38] also show insertion of a metal into the C–H bonds of thiophene. With [(triphos)IrH] (where triphos = $MeC(CH_2PPh_2)_3$) C–H insertion thienyl products are formed at early times of the interaction of [(triphos)IrH] with thiophene, benzothiophene and dibenzothiophene [36]. Platinum-mediated C–H activation in thiophenic substrates has been observed previously in the reaction of [Pt(PEt_3)$_3$] with 4,6-dimethyldibenzothiophene. In this case, the approach of the zerovalent metal complex to the C–S bonds are blocked by the methyl substituents at C-4 and C-6 and the insertion reaction is thus directed to the C–H bond at the 3-position [25].

4. Conclusion

The reaction of 3,6-dimethylthieno[3,2-*b*]thiophene with [Pt(PEt_3)$_4$] yielded a thiaplatinacycle via an oxidative insertion into a C(vinyl)–S bond. While the thiophene-containing molecules 2,2′-bithiophene and 1-methyl-2-(2-thienyl)pyrrole both formed analogous thiaplatinacycles, as deduced from NMR spectra, these molecules also underwent C–H activation to generate *trans*-[PtH(PEt_3)$_2$(2-thienyl)] type complexes. In the case of 1-methyl-2-(2-thienyl)pyrrole it was concluded that the site of C–H activation was at the thienyl rather than the 1-methylpyrrolyl ring.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 214446 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax.: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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