

# The NMR spectroscopic and X-ray crystallographic study of the oxidative addition of bis(2-thienyl) diselenide to zerovalent palladium and platinum centers

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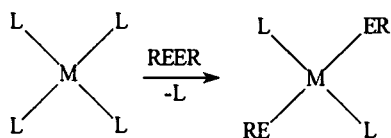
## Abstract

The pathway of the reaction of dithienyl diselenide with tetrakis(triphenylphosphine)palladium(0) and -platinum(0) has been explored by the use of NMR spectroscopy and X-ray diffraction. The oxidative addition of dithienyl diselenide to  $[\text{Pd}(\text{PPh}_3)_4]$  mainly results in the formation of two isomers of dinuclear  $[\text{Pd}_2(\text{SeTh})_4(\text{PPh}_3)_2]$  (Th = 2-thienyl,  $\text{C}_4\text{H}_3\text{S}$ ) complex. The workup of the solution produced X-ray-quality crystals of *trans*- $[\text{Pd}_2(\text{SeTh})_4(\text{PPh}_3)_2]$ . The corresponding reaction with  $[\text{Pt}(\text{PPh}_3)_4]$ , however, affords isomers of mononuclear  $[\text{Pt}(\text{SeTh})_2(\text{PPh}_3)_2]$ . Upon recrystallization from dichloromethane a small amount of crystals of dinuclear  $[\text{Pt}_2(\text{SeTh})_4(\text{PPh}_3)_2]$  is obtained together with those of *trans*- $[\text{Pt}(\text{SeTh})_2(\text{PPh}_3)_2]$ . While the products from both reactions imply that the oxidative addition takes place with the cleavage of the Se–Se bond, a small amount of *trans*- $[\text{PdCl}(\text{Th})(\text{PPh}_3)_2]$  is formed in the reaction of  $[\text{Pd}(\text{PPh}_3)_4]$  and  $\text{Th}_2\text{Se}_2$  in dichloromethane indicating that C–Se cleavage may also take place during the oxidative addition. © 1999 Elsevier Science S.A. All rights reserved.

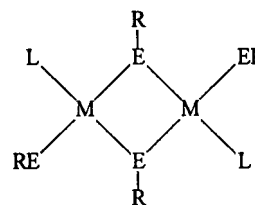
**Keywords:** Aromatic diselenides; Palladium complex; Platinum complex; X-ray crystallography; NMR spectroscopy

## 1. Introduction

The last decade has seen a rapid growth of interest in the coordination chemistry of transition metal complexes with organoselenide and -telluride ligands [1–4] because of their potential utility as precursors for binary transition metal selenides and tellurides, such as  $\text{PdTe}$  and  $\text{NiTe}$  [5–7], which could have applications in the fabrication of new electronic materials [4]. The preparation of these complexes characteristically involves the oxidative addition of the organochalcogen compounds to low-valent transition metal centers most often resulting in the cleavage of the chalcogen–chalcogen bond and the formation of mono- or dinuclear complexes with anionic bridging or terminal  $\text{RE}^-$  (E = Se, Te) ligands:



or



An extensive list of examples is given by Gysling [3] in his comprehensive review on the ligand chemistry of organic selenium and tellurium species. It has, however, also been reported that the reaction of aryl ditellurides with  $\text{Ni}(0)$ ,  $\text{Pd}(0)$ , and  $\text{Pt}(0)$  may result in the cleavage of the carbon–chalcogen bond [8–11]. The oxidative addition of organochalcogen compounds to low-valent transition metal centers is considered a key step in homogeneous catalysis [12].

Chia and McWhinnie [13] deduced in 1978 that the oxidative addition of  $\text{Th}_2\text{Te}_2$  (Th = thienyl,  $\text{C}_4\text{H}_3\text{S}$ ) to  $[\text{Pd}(\text{PPh}_3)_4]$  in benzene solution produces dinuclear  $[\text{Pd}_2(\text{TeTh})_4(\text{PPh}_3)_2]$  with two terminal and two bridging  $\text{ThTe}^-$  ligands. Fukukawa et al. [14] have also reported the formation of an analogous complex

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[Pd<sub>2</sub>(SePh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] from Ph<sub>2</sub>Se<sub>2</sub> and [Pd(PPh<sub>3</sub>)<sub>4</sub>] in benzene. Detailed structural information on the reaction products, however, is missing in both cases. Analogous dinuclear complexes in which two bridging RE<sup>-</sup> (E = S, Se) ligands link two palladium or platinum centers together are exemplified by [Pt<sub>2</sub>I<sub>2</sub>(SCH<sub>2</sub>CMe=CH<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [15], [Pt<sub>2</sub>Cl<sub>2</sub>(SeEt)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] [16], [Pd<sub>2</sub>(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>{Ph<sub>2</sub>P(O)NP(Se)Ph<sub>2</sub>-Se}<sub>2</sub>·2CHCl<sub>3</sub>] [17], [Pd<sub>2</sub>{Se<sub>2</sub>C<sub>8</sub>H<sub>12</sub>}<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [18], and [Pd<sub>2</sub>Cl<sub>2</sub>(SeMe)<sub>2</sub>{SeMe(C<sub>4</sub>H<sub>2</sub>O)}<sub>2</sub>CMe<sub>2</sub>] [19].

We are undertaking a systematic investigation of the oxidative addition of aromatic dichalcogenides to zerovalent palladium and platinum centers. The scope is to gain insight into the factors affecting the actual reaction pathways and product distribution by varying the chemical nature of the chalcogen atom, aromatic substituent, and the solvent. This paper is concerned with the reaction of bis(2-thienyl) diselenide with tetrakis(triphenylphosphine)palladium and -platinum. The reaction products are identified and characterized by X-ray diffraction and NMR spectroscopy.

## 2. Experimental

### 2.1. General

Synthetic work was carried out under a dry argon atmosphere. Tetrahydrofuran and toluene were distilled under nitrogen from Na/benzophenone. Dichloromethane was distilled over CaH<sub>2</sub> and purged with argon before use. Tetrakis(triphenylphosphine)palladium and -platinum (Aldrich) were used without further purification. Dithienyl diselenide was prepared by modifying the literature methods [20].

### 2.2. Syntheses

#### 2.2.1. [Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (1) and [PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] (2)

Dithienyl diselenide (0.100 g, 0.30 mmol) was dissolved in 5 ml of dichloromethane and the resulting solution was added into 20 ml of a dichloromethane solution of [Pd(PPh<sub>3</sub>)<sub>4</sub>] (0.355 g, 0.30 mmol) and stirred overnight. The solution was concentrated by the partial evaporation of dichloromethane. The reaction product was precipitated by adding *n*-hexane to the solution. The red precipitate was filtered off, washed with hexane and dried. Recrystallization from dichloromethane by slow evaporation of the solvent yielded red crystals suitable for X-ray analysis. M.p. (dec.) 152–154°C, yield 0.199 g (95%). Anal. Calc. for C<sub>52</sub>H<sub>42</sub>P<sub>2</sub>Pd<sub>2</sub>S<sub>4</sub>Se<sub>4</sub>: C, 45.07; H, 3.06; S, 9.26. Found: C, 45.73; H, 2.93; S, 9.29%.

Upon slow evaporation of the filtrate a small amount of green crystals of [PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] (2) (0.01 g, yield 5%) was formed.

The preparation was repeated by using toluene as a solvent instead of dichloromethane. The same main product 1 was obtained also in this case.

#### 2.2.2. [Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (3) and [Pt<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (4)

The preparation of 3 was performed in dichloromethane in a similar fashion to that described above for 1 by using 0.065 g (0.20 mmol) of dithienyl diselenide and 0.250 g (0.20 mmol) of [Pt(PPh<sub>3</sub>)<sub>4</sub>]. The product was separated as an orange–yellow precipitate, yield 0.120 g (55%). Anal. Calc. for C<sub>44</sub>H<sub>36</sub>P<sub>2</sub>S<sub>2</sub>Se<sub>2</sub>Pt: C, 50.63; H, 3.48; S, 6.14. Found: C, 50.80; H, 3.36; S, 6.56%. Recrystallization from dichloromethane by a slow evaporation of the solvent yielded yellow crystals of 3·½CH<sub>2</sub>Cl<sub>2</sub> suitable for X-ray analysis. M.p. (dec.) 156–158°C.

In addition to 3 a small amount of yellow crystals of 4 was separated upon recrystallization from dichloromethane.

### 2.3. NMR spectroscopy

The <sup>31</sup>P{<sup>1</sup>H}-, <sup>77</sup>Se- and <sup>195</sup>Pt-NMR spectra were recorded on a Bruker DPX400 spectrometer operating at 161.98, 76.31, and 85.60 MHz, respectively. The typical respective spectral widths were 58.480, 68.493, and 42.735 kHz. The pulse widths were 8.55, 7.30 and 9.20 μs, the two former corresponding to a nuclear tip angle of ca. 45°, and the last to a tip angle of ca. 25°. The <sup>31</sup>P pulse delay was 1.0 s, that for <sup>77</sup>Se was 1.6 s, and that for <sup>195</sup>Pt was 0.5 s. The <sup>31</sup>P accumulations contained ca. 5000–10 000 transients, those for <sup>77</sup>Se 30 000–50 000 transients, and for <sup>195</sup>Pt 10 000 transients. Chloroform-*d* or benzene-*d*<sub>6</sub> was used as a <sup>2</sup>H lock. Orthophosphoric acid (85%), a saturated D<sub>2</sub>O solution of selenium dioxide, and the D<sub>2</sub>O solution of PtCl<sub>6</sub><sup>2-</sup> were used as external standards. The <sup>31</sup>P and <sup>195</sup>Pt chemical shifts are reported relative to the external standard and the <sup>77</sup>Se chemical shifts relative to neat Me<sub>2</sub>Se [ $\delta(\text{Me}_2\text{Se}) = \delta(\text{SeO}_2) + 1302.6$ ].

### 2.4. X-ray crystallography

Diffraction data for 1–4 were collected on a Nonius Kappa CCD diffractometer at 293 K using graphite monochromated Mo-K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by recording 360 frames via  $\phi$ -rotation ( $\Delta\phi = 1^\circ$ ; twice 10–20 s per frame). Crystal data and the details of the structure determinations are given in Table 1.

All structures were solved by direct methods using SHELXS-97 [21] and refined using SHELXL-97 [22]. The terminal ThSe<sup>-</sup> ligands in 1 and 4 were found to be

orientationally disordered, as were both selenium-containing ligands in **3**. It was also observed that the six phenyl rings in **4** could each assume two different orientations. In the refinement the disorder was taken into account, and the site occupation factors of each disordered pair were refined by constraining their sums to unity. Since the site occupation factors and thermal parameters of the disordered atoms correlate with each other, the thermal parameters of the corresponding pairs of atoms were restrained to be equal.

After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions in the aromatic rings (C–H = 0.93 Å). In the final refinement the hydrogen atoms were riding with the carbon atom they were bonded to. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated within the programs. Fractional coordinates, anisotropic thermal parameters, and the full listing of bond parameters are available as supplementary material.

### 3. Results and discussion

#### 3.1. General

The reaction of dithienyl diselenide and [Pd(PPh<sub>3</sub>)<sub>4</sub>] in dichloromethane or toluene produces [Pd<sub>2</sub>(SeTh)<sub>4</sub>-

(PPh<sub>3</sub>)<sub>2</sub>] (**1**) with good yields. In dichloromethane [PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] (**2**) is obtained as a minor side product. Both **1** and **2** are air-stable and soluble in most organic solvents. *Trans*-isomers of both [Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] and [PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] crystallize from dichloromethane or chloroform to yield X-ray quality single crystals.

Dithienyl diselenide reacts with [Pt(PPh<sub>3</sub>)<sub>4</sub>] in a slightly different fashion. The main product in dichloromethane is a mixture of *cis*- and *trans*-isomers of mononuclear [Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (see discussion below). Upon recrystallization from dichloromethane *trans*-[Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**3**) is obtained with a small amount of dinuclear *trans*-[Pt<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**4**).

The structures and identities of the reaction products **1–4** are established by NMR spectroscopy and X-ray crystallography.

#### 3.2. X-ray crystallography

The molecular structures and the numbering of the atoms of *trans*-[Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**1**) and *trans*-[PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] (**2**) are shown in Figs. 1 and 2. Those of *trans*-[Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**3**) and *trans*-[Pt<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**4**) are shown in Figs. 3 and 4. The selected bond distances and angles are listed in Table 2.

All species **1–4** form discrete complexes. The dinuclear complexes **1** and **4** have similar molecular structures, though they are not isostructural. In every complex the palladium or platinum atoms show a

Table 1  
Details of the structure determination of [Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**1**), [PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] (**2**), [Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**3**), and [Pt<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**4**)

	<b>1</b>	<b>2</b>	3·½CH <sub>2</sub> Cl <sub>2</sub>	<b>4</b>
Empirical formula	C <sub>26</sub> H <sub>21</sub> PS <sub>2</sub> Se <sub>2</sub> Pd	C <sub>40</sub> H <sub>33</sub> ClP <sub>2</sub> SPd	C <sub>44.5</sub> H <sub>36</sub> ClP <sub>2</sub> S <sub>2</sub> Se <sub>2</sub> Pt	C <sub>26</sub> H <sub>21</sub> PS <sub>2</sub> Se <sub>2</sub> Pt
Relative molecular mass	692.84	749.51	1085.25	781.53
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	13.279(3)	12.2220(5)	11.209(2)	14.452(3)
<i>b</i> (Å)	16.949(3)	12.7082(5)	34.471(7)	10.671(2)
<i>c</i> (Å)	12.518(3)	13.3445(5)	22.435(4)	18.030(4)
$\alpha$ (°)		90.598(5)		
$\beta$ (°)	111.42(3)	115.039(5)	101.98(3)	111.81(3)
$\gamma$ (°)		108.842(5)		
<i>V</i> (Å <sup>3</sup> )	2623(1)	1750.9(1)	8480(3)	2581.5(9)
<i>Z</i>	4	2	8	4
<i>F</i> (000)	1352	764	4224	1480
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.755	1.422	1.700	2.011
$\mu$ (Mo–K $\alpha$ ) (mm <sup>-1</sup> )	3.716	0.785	5.294	8.492
Crystal size (mm)	0.25 × 0.25 × 0.10	0.40 × 0.15 × 0.08	0.40 × 0.25 × 0.20	0.30 × 0.15 × 0.10
$\theta$ Range (°)	2.04–28.29	2.62–26.42	2.41–25.00	2.97–26.34
Number of observed reflections	2521	4114	5470	3767
[ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]				
Number of parameters/restraints	306/15	402/0	505/40	372/79
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0642	0.0543	0.0377	0.0451
<i>wR</i> <sub>2</sub> <sup>a</sup>	0.1126	0.0804	0.1017	0.1158
Goodness-of-fit	0.912	1.069	1.011	1.022
Max./min. heights in final difference	0.914, –1.552	0.714, –0.382	1.486, –1.298	1.194, –1.257
Fourier synthesis (e Å <sup>-3</sup> )				

<sup>a</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ,  $wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2}$ .

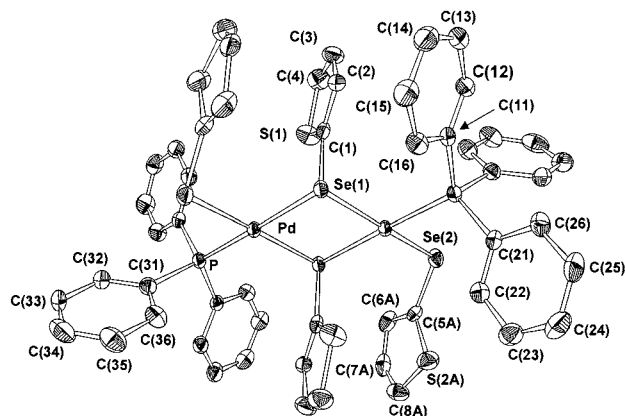


Fig. 1. The molecular structure of [Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (1) indicating the numbering of the atoms. The terminal thienyl rings are disordered. The more favored orientation (A) is shown in the figure (site occupation factor is 0.51). The thermal ellipsoids have been drawn at 30% probability.

slightly distorted square-planar coordination geometry (for the individual bond parameters in the coordination sphere, see Table 2).

In **1** and **4** the two symmetry-related neighboring coordination planes are linked together through two bridging ThSe<sup>-</sup> ligands (see Figs. 1 and 4). This kind of planar [M(μ-SeR)<sub>2</sub>M] (M = Pd, Pt) arrangement is well established [15–17,23]. While both [Pd<sub>2</sub>(Se<sub>2</sub>-C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [18] and [Pd<sub>2</sub>Cl<sub>2</sub>(SeMe)<sub>2</sub>{SeMe-(C<sub>4</sub>H<sub>2</sub>O)}<sub>2</sub>CMe<sub>2</sub>] [19] contain a similar [Pd{μ-SeR}<sub>2</sub>Pd] fragment, there is an angle of 104.4 [18] and 124.5° [19] between the two neighboring coordination planes.

The lengths of the bridging and terminal Pd–Se bonds (2.463(1)–2.466(1) Å) in **1** are close to single bond lengths (the sum of the covalent radii of palladium and selenium is 2.45 Å [24]) and can be compared to the Pd–Se distances of 2.382–2.560 Å in [Pd(C<sub>9</sub>H<sub>12</sub>N){N(SePPh<sub>2</sub>)<sub>2</sub>-Se,Se'}] [17], [Pd<sub>2</sub>(Se<sub>2</sub>C<sub>8</sub>-

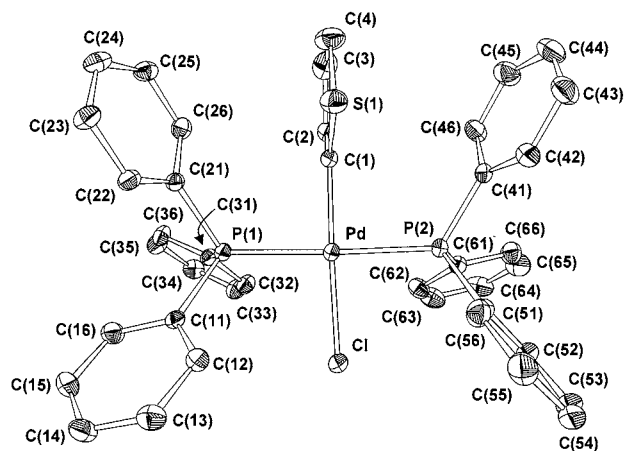


Fig. 2. The molecular structure of [PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] (2) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 30% probability.

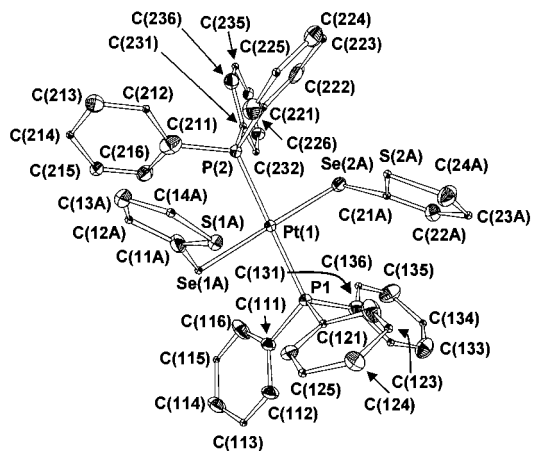


Fig. 3. The molecular structure of [Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (3) indicating the numbering of the atoms. The more favored orientation A of the disordered thienyl rings is shown in the figure (site occupation factor is 0.71). The thermal ellipsoids have been drawn at 30% probability.

H<sub>12</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [18], [Pd{N(SePPh<sub>2</sub>)<sub>2</sub>-Se,Se'}] [25], [Pd<sub>2</sub>Cl<sub>2</sub>(PPr<sup>t</sup>)<sub>2</sub>(SeC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>] [26], and [Pd(C<sub>3</sub>S<sub>3</sub>Se<sub>2</sub>)<sup>-</sup>] [27].

Pt–Se distances in **3** and **4** are 2.4629(1)–2.4651(1) and 2.440(1)–2.508(6) Å, respectively. They are slightly longer than the Pt–Se bonds in [Pt(SeR)<sub>2</sub>L<sub>2</sub>] (R = Ph, py, L = PPh<sub>3</sub>, or L<sub>2</sub> = dppe, dppm) (the average bond lengths range from 2.418 to 2.466 Å; Refs. [28,29]), [Pt<sub>2</sub>Cl<sub>2</sub>(SeEt)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (average 2.430 Å; Ref. [16]), [Pt<sub>2</sub>Se<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (average 2.449 Å; Ref. [23]), and [Pt(Se<sub>2</sub>CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (average 2.426 Å; Ref. [30]).

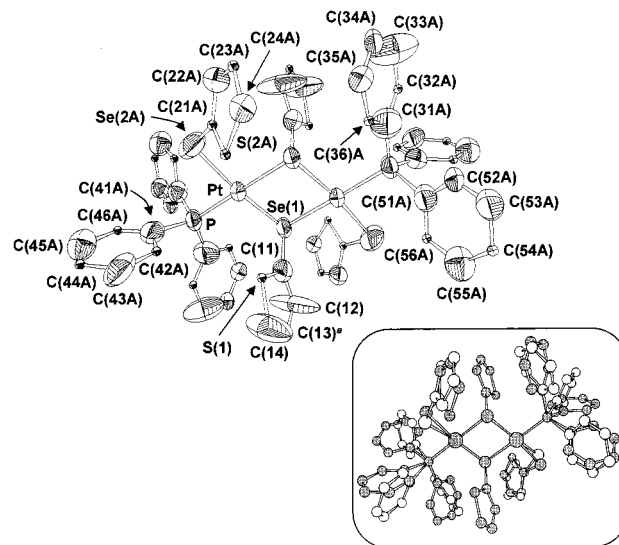


Fig. 4. The molecular structure of [Pt<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (4) indicating the numbering of the atoms. The more favored orientation (A) of the terminal thienyl rings is shown in the figure (site occupation factor is 0.81). The full disorder scheme of both the thienyl and phenyl rings is shown in the insert. The site occupation factors of the two orientations of the phenyl rings are 0.55 and 0.45 for the orientations A and B, respectively. The thermal ellipsoids have been drawn at 30% probability.

Table 2  
Selected bond lengths (Å) and angles (°) for [Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (1), [PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] (2), [Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (3) and [Pt<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (4)

[Pd <sub>2</sub> (SeTh) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] (1)		[PdCl(Th)(PPh <sub>3</sub> ) <sub>2</sub> ] (2)		[Pt(SeTh) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] (3)		[Pt <sub>2</sub> (SeTh) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] (4)	
Pd–Se(1)	2.4661(11)	Pd–Cl	2.3812(12)	Pt–Se(1)	2.4629(1)	Pt–Se(1)	2.4715(10)
Pd–Se(2)	2.4634(12)	Pd–P(1)	2.3438(12)	Pt–Se(2)	2.4651(1)	Pt–Se(2A)	2.4395(13)
Pd–Se(1) <sup>a</sup>	2.4657(12)	Pd–P(2)	2.3301(12)	Pt–P(1)	2.3114(17)	Pt–Se(2B)	2.508(6)
Pd–P	2.297(2)	Pd–C(1)	2.014(3)	Pt–P(2)	2.3204(16)	Pt–Se(1) <sup>b</sup>	2.4461(10)
						Pt–P	2.273(2)
Se(1)–Pd–Se(2)	92.81(4)	Cl–Pd–P(1)	93.26(4)	Se(1)–Pt–Se(2)	179.6(1)		
Se(1)–Pd–Se(1) <sup>a</sup>	83.10(4)	Cl–Pd–P(2)	88.73(4)	Se(1)–Pt–P(1)	83.88(4)	Se(1)–Pt–Se(2A)	92.66(4)
Se(1) <sup>a</sup> –Pd–Se(2)	172.44(4)	Cl–Pd–C(1)	174.78(10)	Se(1)–Pt–P(2)	96.62(4)	Se(1)–Pt–Se(2B)	93.99(14)
Se(1)–Pd–P	177.42(6)	P(1)–Pd–P(2)	176.07(5)	Se(2)–Pt–P(1)	95.94(4)	Se(1)–Pt–Se(1) <sup>b</sup>	81.39(4)
Se(1) <sup>a</sup> –Pd–P	96.60(7)	P(1)–Pd–C(1)	88.47(8)	Se(2)–Pt–P(2)	83.57(4)	Se(1)–Pt–P	178.37(6)
Se(2)–Pd–P	87.77(7)	P(2)–Pd–C(1)	89.27(8)	P(1)–Pt–P(2)	178.20(6)	Se(2A)–Pt–Se(1) <sup>b</sup>	173.51(4)
Pd–Se(1)–Pd <sup>a</sup>	96.90(4)					Se(2B)–Pt–Se(1) <sup>b</sup>	160.9(2)
						Se(2A)–Pt–P	88.77(7)
						Se(2B)–Pt–P	87.62(15)
						P–Pt–Se(1) <sup>b</sup>	97.15(6)
						Pt–Se(1)–Pt <sup>b</sup>	98.61(4)

<sup>a</sup> Symmetry operation:  $-x+1, -y+1, -z+1$ .

<sup>b</sup> Symmetry operation:  $-x+1, -y, -z+2$ .

The Pd–P distances in **1** and **2** (2.297(2) and 2.330(1)–2.344(1), respectively) as well as the Pt–P distances in **3** and **4** (2.311(2)–2.320(2) and 2.273(2) Å) are normal for palladium–phosphorus or platinum–phosphorus bonds. The small differences can be explained by the effects of relative *trans*-influence. The bond lengths within the ligands are also normal.

The terminal thienyl rings in **1** and **4**, and both thienyl rings in **3** are disordered (see Figs. 1, 3 and 4). In the case of **1** the rings assume two different orientations at the ca. 50% level of probability. In **3** and **4** one orientation is more favored than the other. The thienyl rings of the bridging ligands, on the other hand, are not disordered either in **1** or **4**. The difference may be explained by weak hydrogen bonds that fix the orientation. There are no such close contacts in the terminal ligands, and the thienyl ring assumes two different orientations with almost an equal probability. The thienyl ring in **2** also finds itself in a fixed orientation with no indication of disorder due to the weak hydrogen bonds.

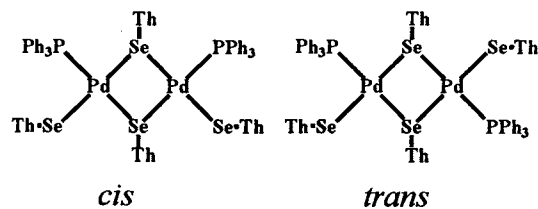
### 3.3. NMR spectroscopy

#### 3.3.1. The reaction of [Pd(PPh<sub>3</sub>)<sub>4</sub>] and Th<sub>2</sub>Se<sub>2</sub>

The reaction of [Pd(PPh<sub>3</sub>)<sub>4</sub>] and Th<sub>2</sub>Se<sub>2</sub> in dichloromethane rapidly produces a mixture exhibiting three major <sup>31</sup>P resonances at 29.9, 29.3, and –3.6 ppm. Upon prolonged standing a new resonance appears at 25.0 ppm.

The workup of the reaction mixture produced a precipitate that upon redissolution exhibited only two resonances at 29.9 and 29.3 ppm. It was inferred that

these resonances are due to the *cis*- and *trans*-isomers of [Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>]. The recrystallization afforded *trans*-[Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**1**).



The <sup>77</sup>Se-NMR spectrum of the redissolved precipitate exhibited two resonances at 203 and 198 ppm due to terminal ThSe<sup>–</sup> ligands and three resonances at –163, –180 and –182 ppm due to bridging ligands. *cis*-[Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] is expected to exhibit three resonances at the intensity ratio of 2:1:1. The first resonance corresponds to two equivalent terminal ligands. The two latter signals each correspond to one independent bridging ligand. In the *trans*-isomer both terminal and bridging ligands are mutually symmetry-equivalent, and only two resonances are expected in the intensity ratio of 1:1.

The strongest signal at 198 ppm has approximately twice the intensity of the other four resonances and is assigned to two terminal ligands of *cis*-[Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>]. The signal at 203 ppm must then be due to the *trans*-isomer. The assignment of the remaining signals to the bridging ligands of the two isomers can be carried out by considering the effects of the *trans*-influence on the chemical shifts and on the coupling information (see Ref. [31]).

It can be concluded that *cis*-[Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] exhibits three resonances at 198, –163 (<sup>2</sup>J<sub>Pse</sub> = 137 Hz),

and  $-182$  ppm with the intensity ratio of 2:1:1. *trans*-[Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] shows two resonances of equal intensity at 203 and  $-180$  ppm.

The filtrate after the hexane precipitation was found to exhibit two <sup>31</sup>P-NMR resonances at 25.0 and  $-3.6$  ppm. The former is due to the mononuclear complex [PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] (**2**), and latter is due to free PPh<sub>3</sub>.

When the reaction of [Pd(PPh<sub>3</sub>)<sub>4</sub>] and Th<sub>2</sub>Se<sub>2</sub> was carried out in toluene, the <sup>31</sup>P-NMR spectrum of the reaction mixture exhibited the two resonances due to the isomers of the dinuclear palladium complex **1** together with free PPh<sub>3</sub>.

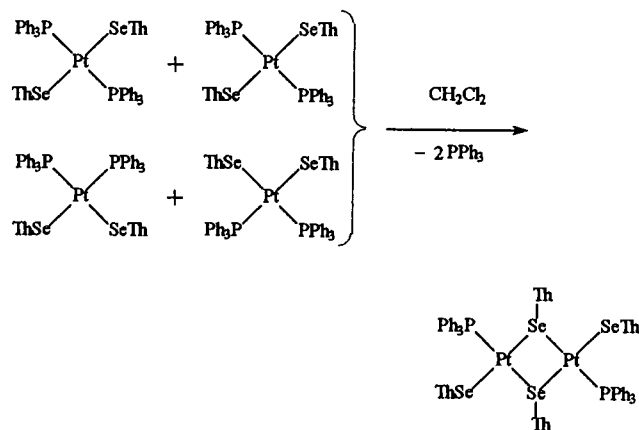
### 3.3.2. The reaction of [Pt(PPh<sub>3</sub>)<sub>4</sub>] and Th<sub>2</sub>Se<sub>2</sub>

The <sup>31</sup>P spectrum of the reaction mixture of [Pt(PPh<sub>3</sub>)<sub>4</sub>] and Th<sub>2</sub>Se<sub>2</sub> in dichloromethane shows two major <sup>31</sup>P-NMR resonances at 21.5 and 17.9 ppm with satellites due to coupling to <sup>195</sup>Pt. The respective coupling constants are 2864 and 3070 Hz that are typical for <sup>1</sup>J<sub>PtP</sub> [4]. In addition the solution contains some Ph<sub>3</sub>PSe (37 ppm), Ph<sub>3</sub>PO (30 ppm), and free PPh<sub>3</sub>.

Yellow crystals of *trans*-[Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**3**) show one resonance at 21.5 ppm (<sup>1</sup>J<sub>PtP</sub> = 2864 Hz). The resonance at 17.9 ppm (<sup>1</sup>J<sub>PtP</sub> = 3070 Hz) is assigned to *cis*-[Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]. This is consistent with the reported chemical shifts of *trans*- and *cis*-[Pt(SePh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] in benzene-*d*<sub>6</sub> (20.6 ppm (<sup>1</sup>J<sub>PtP</sub> = 2831 Hz) and 18.4 ppm (<sup>1</sup>J<sub>PtP</sub> = 2969 Hz), respectively) [32]. It was observed that upon prolonged standing in dichloromethane, the intensity of the resonance at 17.9 ppm decreases with respect to the resonance at 21.5 ppm. The <sup>195</sup>Pt chemical shift of *cis*-[Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] is  $-4859$  ppm (<sup>1</sup>J<sub>PtP</sub> = 3068 Hz) and that of *trans*-[Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]  $-4937$  ppm (<sup>1</sup>J<sub>PtP</sub> = 2858 Hz).

The <sup>77</sup>Se-NMR spectrum of the initial reaction mixture of [Pt(PPh<sub>3</sub>)<sub>4</sub>] and Th<sub>2</sub>Se<sub>2</sub> in dichloromethane exhibits two resonances at 171 and 80 ppm with an approximate intensity ratio of 1:2. The intensity of the resonance at 171 ppm decreases with time. The resonance at 80 ppm due to *trans*-[Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**3**) shows two <sup>195</sup>Pt satellites (<sup>1</sup>J<sub>PtSe</sub> = 117 Hz). All three components are further split into triplets (<sup>2</sup>J<sub>PSe</sub> = 14 Hz). The coupling information is well in accord with that reported for [Pt(SeC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>(dppe)] [26]: <sup>1</sup>J<sub>PtP</sub> = 2968, <sup>1</sup>J<sub>PtSe</sub> = 220, <sup>2</sup>J<sub>PSe(cis)</sub> = 12 Hz. The resonance at 171 ppm is assigned to *cis*-[Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>].

Upon recrystallization of **3**, a small amount of crystalline *trans*-[Pt<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**4**) was simultaneously obtained. These crystals were hand-picked under a microscope (<sup>31</sup>P resonance at 20.4 ppm (<sup>1</sup>J<sub>PtP</sub> = 3422 Hz); <sup>77</sup>Se resonances at 163 and  $-169$  ppm) and were structurally characterized (see Section 3.2). **4** is probably slowly formed either from two *trans*- or two *cis*-isomers of [Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]:



## 4. Conclusions

This paper reports the reactions of tetrakis-(triphenylphosphine)palladium and -platinum with bis(thienyl) diselenide as part of a systematic investigation of the factors affecting the pathways of oxidative addition of aromatic dichalcogenides to zerovalent palladium and platinum centers. The oxidative addition to both [Pd(PPh<sub>3</sub>)<sub>4</sub>] and [Pt(PPh<sub>3</sub>)<sub>4</sub>] results in the cleavage of the Se–Se bond. The main products in the reaction of [Pd(PPh<sub>3</sub>)<sub>4</sub>] and Th<sub>2</sub>Se<sub>2</sub> are dinuclear *cis*- and *trans*-[Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>], which could be identified by <sup>31</sup>P- and <sup>77</sup>Se-NMR spectroscopy. Recrystallization afforded *trans*-[Pd<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>], which could be characterized by X-ray crystallography. When the reaction is carried out in dichloromethane, a small amount of [PdCl(Th)(PPh<sub>3</sub>)<sub>2</sub>] is formed. This implies that the solvent plays an active role in the reaction and that the cleavage of a C–Se bond may also occur during the oxidative addition. A number of analogous palladium and platinum complexes are formed in different oxidative addition reactions (see Refs. [11,33–36]). It has been suggested by Xie et al. [37] that the formation of species like **2** plays an important role in the catalytic activity of palladium and platinum complexes.

The reaction of [Pt(PPh<sub>3</sub>)<sub>4</sub>] also results in the cleavage of the Se–Se bond in Th<sub>2</sub>Se<sub>2</sub>, but in this case the reaction mixture contained the *cis*- and *trans*-isomers of the mononuclear complex [Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]. Crystals of *trans*-[Pt(SeTh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] were obtained upon recrystallization from dichloromethane. Simultaneously, small amounts of dinuclear *trans*-[Pt<sub>2</sub>(SeTh)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] were obtained.

The route of the oxidative addition of aromatic diselenides proceeds somewhat differently, depending on whether [Pd(PPh<sub>3</sub>)<sub>4</sub>] or [Pt(PPh<sub>3</sub>)<sub>4</sub>] is used as a reagent. The different behavior of analogous palladium and platinum complexes has very recently been noted for the reactions of [MCl<sub>2</sub>(PhCN)<sub>2</sub>] (M = Pd, Pt) with cyclohepteno-1,4-diselenin [18,38]. The reaction with

[PdCl<sub>2</sub>(PhCN)<sub>2</sub>] is a simple ligand substitution reaction whereas with [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] an oxidative addition of a C–Se bond to a Pt(II) center takes place with the formation of a dinuclear platinum(IV) complex.

The oxidative addition reactions involving aromatic ditellurides are significantly more complicated than those involving diselenides. They also depend on the choice of the aromatic substituent, and are sensitive to the choice of the solvent. The work to understand the factors governing the reaction pathway is currently in progress.

## 5. Supplementary material

Crystallographic information for complexes **1–4** (excluding tables of structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CSD-118899–118902, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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