Available online at www.sciencedirect.com

Journal of Organometallic Chemistry 678 (2003) 95–101

www.elsevier.com/locate/jorganchem

$C_4H_3SSeCH_2CH_2OC_6H_5$: synthesis, characterization and reaction with palladium(II) and nickel(II)

Raija Oilunkaniemi [a,*], Risto S. Laitinen [a], Milja S. Hannu-Kuure [a], Markku Ahlgrén [b]

[a] *Department of Chemistry, University of Oulu, P.O. Box 3000, FIN-90014 Oulu, Finland*
[b] *Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland*

Received 7 March 2003; received in revised form 13 May 2003; accepted 14 May 2003

Abstract

$ThSeCH_2CH_2OPh$ (Th = 2-thienyl, C_4H_3S-; Ph = phenyl) (**2**) has been prepared by the reaction of $BrCH_2CH_2OPh$ (**1**) and ThSeLi. The compound was characterized by $^{13}C\{^1H\}$- and ^{77}Se-NMR spectroscopy and X-ray crystallography. **2** is monoclinic, space group $P2_1/c$, $a = 10.865(2)$, $b = 5.152(1)$, $c = 41.996(8)$ Å, $\beta = 92.20(3)°$. All bond lengths and angles are quite normal as exemplified by the respective Se–C(alkyl) and Se–C(aryl) bonds of 1.957(6)–1.966(6) and 1.901(7)–1.905(7) Å. The lattice is composed of discrete molecules that are joined together by weak hydrogen bonds into a three-dimensional network. Upon treating $ThSeCH_2CH_2OPh$ with $[PdCl_2(NCPh)_2]$ and $[NiCl_2(PPh_3)_2]$ in benzene, a dinuclear palladium complex $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeTh)(PPh_3)_2]$ (**3**) and a mononuclear complex $[PdCl_2(PPh_3)_2]$ (**4**) were formed together with a precipitation of $NiCl_2$. The X-ray quality crystals were recrystallized in CH_2Cl_2. $\mathbf{3}\cdot 2.5CH_2Cl_2$ is monoclinic, space group $C2/c$, $a = 32.907(7)$, $b = 14.545(3)$, $c = 22.433(5)$ Å, $\beta = 114.37(3)°$ and contains a novel asymmetrical arrangement of one bridging chlorido and thienylselenolato ligand. Both palladium atoms show an square-planar coordination. The terminal Pd–Cl bond lengths are 2.388(1) and 2.346(1) Å with slightly longer distances of 2.418(1) and 2.450(1) Å involving the bridging chlorido ligand. The Pd–Se distances are 2.4092(9) and 2.4376(7) Å.

Keywords: 2-Phenoxyethylthienylselenide; Palladium complex; X-ray crystallography; NMR spectroscopy

1. Introduction

Selenoethers contain a soft donor atom and can therefore easily coordinate with soft transition metal centers such as palladium and platinum, and there is a number of reports on the formation and structural characterization of complexes containing mono- and polyselenoethers (for recent reviews, see Refs. [1–5] and references therein).

The solid state structural chemistry of hybrid polydentate selenoether complexes of palladium and platinum is very sparse (for the most recent review, see Ref. [5]). The two platinum atoms in $[(PtMe_2)_2\{\mu\text{-}(H_2C{=}CH{-}CH_2{-}CH_2)_2Se\}]$ are bridged by the selenoether ligand that coordinates to one Pt(II) center through a selenium donor and to another Pd(II) center involving the π-electrons of the terminal C=C bond [6]. $[PtCl_2(PhSeCH_2CH_2NMe_2)]$ contains a chelating ligand coordinating both through a selenium and a nitrogen donor [7]. The tridentate ligand in chlorido{(4-methyl-2-phenylselenyl)phenylazo-*p*-toluene}palladium involves a selenium, nitrogen and C^- donor in the coordination [8].

There are only a very few reports on the hybrid complexes containing different Group 16 donor atoms. In fact, there are examples that the selenium-containing crown ethers coordinate only through selenium and not through the ether oxygen atom [9–11]. One of the very few examples exhibiting simultaneous selenium and oxygen coordination is $[Pd(Ph)(PPh_3)(MeSeCH_2COO)]$ [12].

The lightest metal of the Group 10 elements, nickel, shows very few selenoether complexes. X-ray structures have only been established for $[NiCl_2(MeSeCH_2CH_2$-

---

* Corresponding author. Tel.: +358-8-553-1686; fax: +358-8-553-1608.
E-mail address: raija.oilunkaniemi@oulu.fi (R. Oilunkaniemi).

0022-328X/03/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00450-9

SeMe)]$_2$ [13] and [{C_5H_3N)CH_2SeCH_2-*N*,*Se*}$_2(OH_2)_2$-Ni][ClO_4]·$MeNO_2$ [14] that both exhibit an octahedral coordination around nickel.

The goal of the present contribution was to explore whether a hybrid selenoether ligand containing a C–O–C moiety could be utilized as a bridging ligand in the formation of a heteronuclear complex containing Group 10 metals nickel and palladium. In this paper we report the preparation and structural characterization of $ThSeCH_2CH_2OPh$ (Th = 2-thienyl, C_4H_3S) as well as some of its ligand properties. The X-ray structure of $PhOCH_2CH_2Br$ that is one of the starting materials in the synthesis of $ThSeCH_2CH_2OPh$ has been reported for comparison.

2. Experimental

2.1. General

$PhOCH_2CH_2Br$ (**1**, Aldrich), *n*-butyllithium (2.5 M solution in hexanes, Aldrich), thiophene (Riedel de Haen, dried and distilled prior to use), selenium (granules, Merck), and $NiCl_2$ (Merck) were commercially available. [$PdCl_2(PhCN)_2$] was synthesized by modifying the method of Kharasch et al. [15] and [$NiCl_2(PPh_3)_2$] by the method of Venanzi [16].

2.2. Preparation of $ThSeCH_2CH_2OPh$ (2)

n-BuLi (2.5 M, 6.00 ml; 15.0 mmol) was added into a solution of 1.5 ml (17.0 mmol) of thiophene in 25 ml of tetrahydrofuran that was cooled in an ice bath. The mixture was stirred at room temperature (r.t.) for 1 h. Powdered selenium (1.35 g; 17.0 mmol) was added to the solution under a nitrogen flow and the mixture was stirred at r.t. for an additional hour. $PhOCH_2CH_2Br$ (3.44 g, 17.0 mmol) was gradually added into the reaction mixture in small portions. After 30 min the reaction mixture was poured into water (150 ml), the product was extracted in dichloromethane (3 × 50 ml), and the organic layer was dried with $MgSO_4$. The yield of $ThSeCH_2CH_2OPh$ in the product mixture was ca. 85% (based on selenium), as judged by the ^{77}Se-NMR spectrum recorded in the CH_2Cl_2 solution. The solvent was removed upon evaporation and the oily residue was dissolved in hexane and cooled to −20°. The resulting pale yellow precipitate was filtered cold, washed several times with cold hexane, and dried. Small colourless crystals were obtained from ethanol by slow evaporation of the solvent. Yield of the purified product: 2.31 g (54%). Anal. calc. for $C_{12}H_{12}OSSe$: C 50.88, H 4.27, S 11.32; found: C 49.86, H 4.04, S 10.89%. NMR (298 K, CH_2Cl_2): ^{77}Se $\delta = 183$ ppm, $^2J_{Se-H}$ 15.2 Hz, $^3J_{Se-H}$ 5.1 Hz; $^{13}C\{^1H\}$: 29.4 [*1C*; *C*(*n*18)]; 67.0 [*1C*; C(*n*17)]; 114.6 [*2C*; C(*n*12), C(*n*16)]; 120.9 [*1C*; C(*n*14)]; 122.7 [*1C*; C(*n*1)]; 128.1 [*1C*; C(*n*3)]; 129.5 [*2C*; C(*n*13), C(*n*15)]; 131.0 [*1C*; C(*n*2)]; 136.2 [*1C*; C(*n*4)]; 158.3 ppm [*1C*; C(*n*11)] (*n* = 1 or 2; for numbering of the atoms, see Fig. 2).

2.3. Complexation of $ThSeCH_2CH_2OPh$ with Pd(II) and Ni(II)

$ThSeCH_2CH_2OPh$ (**2**) (51 mg, 0.18 mmol) was dissolved in 5 ml of benzene and the resulting solution was added into 5 ml of a benzene solution containing 32 mg (0.083 mmol) of [$PdCl_2(PhCN)_2$]. Subsequently, 53 mg (0.081 mmol) of [$NiCl_2(PPh_3)_2$] in 5 ml of benzene was added into the reaction mixture. The pale green precipitate was filtered off and the solution was concentrated by evaporation upon stirring overnight during which a yellow precipitate was formed. After filtration, the raw product was recrystallized from dichloromethane. Crystals of [$Pd_2Cl_2(\mu\text{-Cl})(\mu\text{-SeTh})(PPh_3)_2$]·$2.5CH_2Cl_2$ (**3**·$2.5CH_2Cl_2$) and [$PdCl_2(PPh_3)_2$]·$2CH_2Cl_2$ (**4**·$2CH_2Cl_2$) were separated from the solid mixture under a microscope and identified by X-ray crystallography. NMR (298 K, CH_2Cl_2): $^{31}P\{^1H\}$ $\delta = 33.9$ ppm (**3**), $\delta = 24.0$ ppm (**4**).

2.4. NMR spectroscopy

The NMR spectra were recorded on a Bruker DPX 400 operating at 100.61, 76.31 and 161.98 MHz for $^{13}C\{^1H\}$, ^{77}Se and $^{31}P\{^1H\}$, respectively. Saturated solution of SeO_2 (aq) was used as an external standard for the ^{77}Se spectra and H_3PO_4 (85%) was used as an external standard for the ^{31}P spectra. Chemical shifts (ppm) are reported relative to Me_4Si, neat Me_2Se and H_3PO_4 (85%). {$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$) [17]}.

2.5. X-ray crystallography

Diffraction data of **1**, **2**, $2.5CH_2Cl_2$ and **4**·$2CH_2Cl_2$ were collected on a Nonius Kappa CCD diffractometer at 150 K using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Crystal data and the details of structure determination are given in Table 1.

Structures were solved by direct methods using SHELXS-97 [18] and refined using SHELXL-97 [19]. The thienyl rings in **2** were found to be disordered. The disorder was taken into account by refining the site occupation factors of the two alternative orientations and constraining their sums to unity. Because the thermal parameters of the disordered atoms correlate with the site occupation factors, the thermal parameters of the disordered pairs of atoms were restrained to be equal.

After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal para-

Table 1
Details of the structure determination of $PhOCH_2CH_2Br$ (**1**), $ThSeCH_2CH_2OPh$ (**2**), $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeTh)(PPh_3)_2]$ (**3**) and *trans*-$[PdCl_2(PPh_3)_2]$ (**4**)

	1	**2**	**3**·$2.5CH_2Cl_2$	**4**·$2CH_2Cl_2$
Empirical formula	C_8H_9BrO	$C_{24}H_{24}O_2S_2Se_2$	$C_{42.5}H_{38}Cl_8P_2SSePd_2$	$C_{19}H_{17}Cl_3PPd_{0.5}$
Relative molecular mass	201.06	283.24	1218.09	435.85
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*C*2/c	*P*2₁/*c*	*C*2/c	*Pbca*
Unit cell dimensions				
a (Å)	19.049 (4)	10.865(2)	32.907(7)	20.122(4)
b (Å)	5.478(1)	5.1522(1)	14.545(3)	7.994(2)
c (Å)	15.536(3)	41.996(8)	22.433(5)	23.032(5)
β (°)	98.79(3)	92.20(3)	114.37(3)	
V ($Å^3$)	1602.1(6)	2349.1(8)	9781(3)	3705(1)
Z	8	4	8	8
F(0 0 0)	800	1136	4808	1760
D_{calc} ($g\ cm^{-3}$)	1.667	1.602	1.654	1.563
μ(Mo–K_α) (mm^{-1})	5.058	3.344	2.055	1.048
Crystal size (mm)	0.20 × 0.12 × 0.10	0.35 × 0.15 × 0.08	0.20 × 0.15 × 0.12	0.15 × 0.12 × 0.10
θ range (°)	3.16–25.98	3.01–25.00	2.33–26.00	2.69–29.13
Number of reflections collected	2951	11555	42763	38631
Number of unique reflections	1569	3819	8789	4726
Number of observed reflections [a]	1464	2970	6430	3614
Number of parameters/restraints	92/0	274/20	549/5	215/0
R_{int}	0.0160	0.0839	0.0412	0.0534
R_1 [b]	0.0340	0.0561	0.0358	0.0337
wR_2 [b]	0.1098	0.1413	0.0712	0.0762
R_1 (all data)	0.0363	0.0750	0.0597	0.0549
wR_2 (all data)	0.1135	0.1543	0.0799	0.0847
Goodness-of-fit on F^2	1.016	1.101	1.027	1.024
Max/min heights in final difference Fourier synthesis (e $Å^{-3}$)	0.557, −0.728	0.514, −0.622	0.824, −0.699	0.688, −0.921

[a] $I > 2\sigma(I)$.

[b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

meters, the hydrogen atoms were placed in calculated positions in the aromatic rings (C–H = 0.95 Å and in the CH_2 groups (C–H = 0.99 Å). The scattering factors for the neutral atoms were those incorporated with the programs.

3. Results and discussion

3.1. Preparation of $ThSeCH_2CH_2OPh$ (2)

The reaction of $BrCH_2CH_2OPh$ (**1**) with ThSeLi in THF produced $ThSeCH_2CH_2OPh$ (**2**) in a good yield. The ^{77}Se-NMR spectrum of the reaction mixture shows a major resonance at 183 ppm together with minor resonances at 492, 459, 323, 289 and 258 ppm.

The isolated and purified $ThSeCH_2CH_2OPh$ shows only one resonance at 183 ppm that appears as a triplet of triplets ($^2J_{Se\text{–}H} = 15.2$ Hz, $^3J_{Se\text{–}H} = 5.1$ Hz). The assignment of the ten ^{13}C chemical shifts of purified $ThSeCH_2CH_2OPh$ has been based on those from $BrCH_2CH_2OPh$ (**1**) [20] and Th_2Se_2 [21].

The minor resonance at 492 ppm is due to Th_2Se_2 [21] and the triplet at 459 ppm ($^2J_{Se\text{–}H} = 15.9$ Hz) is assigned to $(PhOCH_2CH_2Se)_2$ that has previously been isolated in an analogous reaction when treating FuSeLi (Fu = C_4H_3O, furyl) with $PhOCH_2CH_2Br$ [22]. The broad singlet at 258 ppm is assigned to Th_2Se based on the well-established relationship between the ^{77}Se and ^{125}Te chemical shifts in analogous compounds [23–26] and on the known ^{125}Te chemical shift of Th_2Te at 402 ppm [27]. The quintet at 289 ppm ($^2J_{Se\text{–}H} = 16$ Hz) is assigned to $(PhOCH_2CH_2)_2Se$.

3.2. Crystal structures

3.2.1. $BrCH_2CH_2OPh$ (1) and $ThSeCH_2CH_2OPh$ (2)

The molecular structures of $PhOCH_2CH_2Br$ (**1**) and $ThSeCH_2CH_2OPh$ (**2**) indicating the numbering of the atoms are shown in Figs. 1 and 2 together with the selected bond lengths and angles.

Both compounds show quite normal bond parameters. The PhOCC frameworks in **1** and **2** are approximately planar and show a similar conformation. It is interesting to note that while Br(1) in **1** deviates from this plane [the torsional angle O(1)–C(7)–C(8)–Br(1) is 68.5(2)°; for numbering of atoms, see Fig. 1], the corresponding selenium atoms Se(11) and Se(21) in **2** lie approximately on the plane (the torsional angles O(*n*1)–C(*n*17)–C(*n*18)–Se(*n*1) are 173.9(4) and 174.1(4)°; for

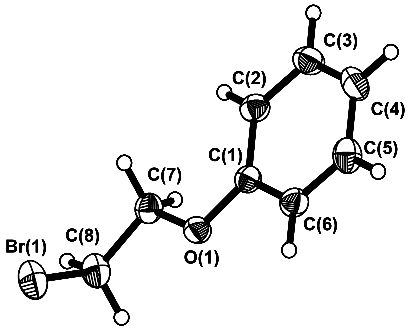


Fig. 1. The molecular structure of $PhOCH_2CH_2Br$ (**1**) indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level. Selected bond lengths (Å) and angles (°): C(1)–O(1) 1.373(3); O(1)–C(7) 1.430(3); C(7)–C(8) 1.502(3); C(8)–Br(1) 1.960(3); C(1)–O(1)–C(7) 117.5(2); O(1)–C(7)–C(8) 107.6(2); C(7)–C(8)–Br(1) 111.0(2).

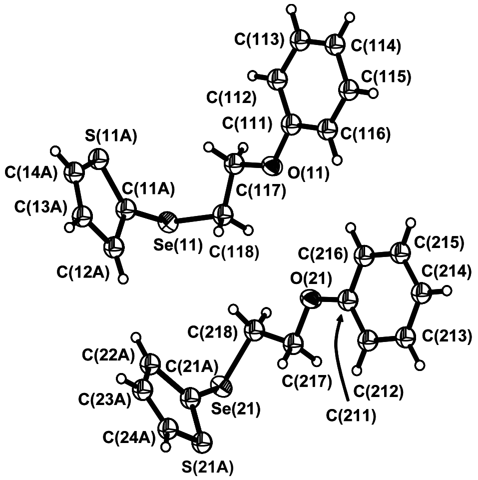
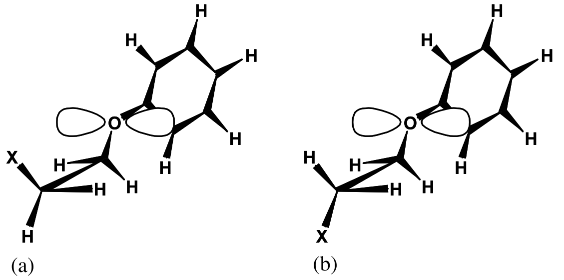


Fig. 2. The two molecules of $PhOCH_2CH_2SeTh$ (**2**) in the asymmetric unit indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level. Selected bond lengths (Å) and angles (°): C(n11)–O(n1) 1.376(7), 1.372(7); O(n1)–C(n17) 1.441(7), 1.450(7); C(n17)–C(n18) 1.507(8), 1.509(9); C(n18)–Se(n1) 1.957(6), 1.966(6); Se(n1)–C(n1A/B) 1.901(7), 1.905(7); C(n11)–O(n(1)–C(n17) 118.5(4), 117.9(4); O(n1)–C(n17)–C(n18) 104.6(5), 104.7(5); C(n17)–C(n18)–Se(n1) 113.0(4), 111.6(4): C(n18)–Se(n1)–C(n1A/B) 96.6(3), 96.2(3). The first value in each pair refers to molecule 1 ($n = 1$) and the second value to molecule 2 ($n = 2$).



(a) (b)

Fig. 3. The two possible orientations of the X group in $PhOCH_2CH_2X$ (X = Br and SeTh) due to steric requirements. The 2p lone pair orbital of the oxygen atom is indicated in the figure. Its minimized repulsion with the π-electrons of the phenyl ring requires a planar PhOCC framework.

numbering of atoms, see Fig. 2). The planarity of the PhOCC fragment and the two possible orientations of the X atom bonded to it (X = Br or Se) can be explained by steric and electronic factors, as shown in Fig. 3. One of the oxygen lone-pairs is in a 2p orbital and necessitates the C–O–C–C torsional angle of ca. 0° for minimized repulsion between these lone-pair electrons and the π-electrons of the phenyl ring. Further, there are two possible orientations for the CH_2X group to be staggered with respect to the CH_2O group that is directly bonded to it. One leads to the OCCX torsional angle of ca. 60° and the other to the torsional angle of ca. 180°, as indicated in Fig. 3. The bromine atom in **1** exhibits the former orientation and the selenium atoms in **2** the latter.

The thienyl groups in both independent molecules of **2** are disordered. The more abundant orientations with site occupation factors of 62.4(9) and 55.1(8)% for molecules 1 and 2, respectively, are shown in Fig. 2. In both molecules the thienyl ring is almost perpendicular to the Se(n1)–C(n18) bond. The angles between the planes of thienyl groups and the Se(n1)–C(n18) bonds in the two molecules are 75.7(2) and 70.8(2)° in qualitative agreement with the values 86.2 and 85.0° between the plane of the aromatic ring and Se–Se bonds in Th_2Se_2 and Fu_2Se_2 [21]. In diselenides, however, the magnitude of this angle is dependent on the electronic and steric factors of the aromatic ring (see discussion and reference in Ref. [21]).

The molecules in both **1** and **2** are joined together into a continuous three-dimensional network by weak hydrogen bonds, as shown in Fig. 4. The shortest H···O contacts show values of 2.660(2) and 2.671(4)–2.693(4) Å for **1** and **2**, respectively. In addition, there are short contacts in both **1** and **2** involving the interaction between the methylene hydrogen atoms and the π-electrons of the phenyl rings.

3.2.2. *cis*-$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeTh)(PPh_3)_2]$ (3) and *trans*-$[PdCl_2(PPh_3)_2]$ (4)

The molecular structure and the numbering of the atoms of $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeTh)(PPh_3)_2]$ (**3**) is shown on Fig. 5. The crystal structure of **3** is the first example of the asymmetric selenolato- and chlorido-bridged dipalladium structure. The syntheses and NMR data for the similar complexes have been reported previously [28–31], but X-ray structures are known neither for palladium nor the related platinum complexes. The sulfur analogues of the palladium complexes form a better explored series [32–35].

The lattice of $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeTh)(PPh_3)_2]\cdot 2.5CH_2Cl_2$ ($\mathbf{3}\cdot 2.5CH_2Cl_2$) is composed of planar discrete dinuclear complexes with the terminal chlorido-ligands in *cis*-positions with respect to each other. Selected bond

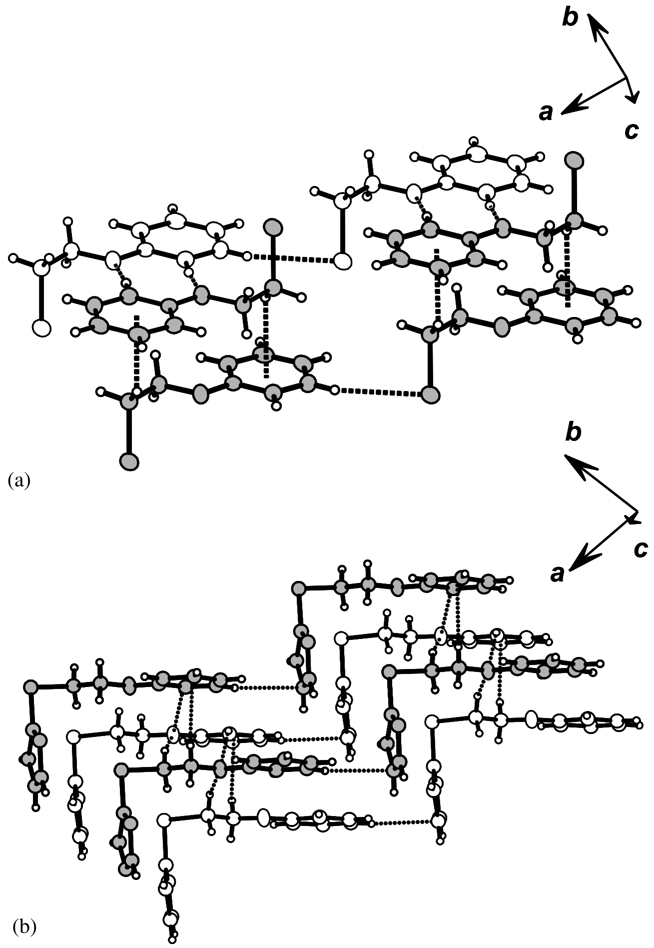


Fig. 4. Hydrogen bonding network in (a) $BrCH_2CH_2OPh$ and (b) $ThSeCH_2CH_2OPh$.

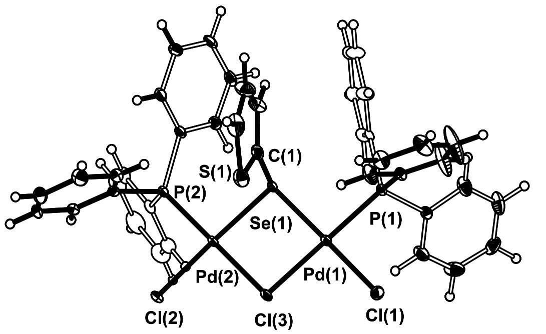


Fig. 5. The molecular structure of *cis*-$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeTh)(PPh_3)_2]$ (**3**) indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level.

lengths and angles are listed in Table 2. Both palladium atoms show a slightly distorted square-planar coordination geometry [the sums of bond angles are 360.13(5) and 360.08(4)° for Pd(1) and Pd(2), respectively]. The terminal Pd–Se bond lengths are slightly smaller than the bridging Pd–Se distances in $[Pd_2(\mu\text{-}SeTh)_2(SeTh)_2(PPh_3)_2]$ [36] and $[Pd_2(\mu\text{-}SePh)_2(SePh)_2(PPh_3)_2]$ [37]. This is consistent with the slightly weaker *trans*-influence of Cl^--ligand compared to those of RSe^- and Ph_3P. The terminal Pd–Cl bonds are also shorter than the bridging Pd–Cl bonds. These bond lengths are comparable to the bridging and terminal Pd–Cl bonds in μ-thiolato complexes $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SR)(PR'_2R'')_2]$ (R = Et; R′ = Me; R″ = Ph [32]; R = Me, *t*-Bu, Ph; R′ = R″ = Me [34]).

The crystal and molecular structure of $\mathbf{4}\cdot 2CH_2Cl_2$ was determined in order to assign the $^{31}P\{^1H\}$ resonance at 24.0 ppm. The structural features of $[PdCl_2(PPh_3)_2]$ crystallized from different solvents have been reported for several times [38–42]. A recent report by Vicente et al. [42] described the structure of exactly the same crystalline phase $\mathbf{4}\cdot 2CH_2Cl_2$, as we have observed in this work (see Table 2).

3.3. Ligand chemistry of $ThSeCH_2CH_2OPh$

When $ThSeCH_2CH_2OPh$ (**2**) was treated with a benzene solution of $[PdCl_2(PhCN)_2]$ and a solution of $[NiCl_2(PPh_3)_2]$ was subsequently added into the reaction mixture (the molar ratio of the reactants was ca. 2:1:1), the red colour of the solution disappeared and the solution became yellow. At the same time a pale green precipitate of $NiCl_2$ was obtained. The $^{31}P\{^1H\}$-NMR spectrum of the reaction solution showed two resonances at 33.9 and 24.0 ppm. Upon recrystallization from dichloromethane, crystals of $[Pd_2Cl_2(\mu\text{-}Cl)(\mu SeTh)(PPh_3)_2]\cdot 2.5CH_2Cl_2$ ($\mathbf{3}\cdot 2.5CH_2Cl_2$) and $[PdCl_2(PPh_3)_2]\cdot 2CH_2Cl_2$ ($\mathbf{4}\cdot 2CH_2Cl_2$) were obtained. The redissolved crystals indicated that the $^{31}P\{^1H\}$ resonance at 33.9 ppm is due to **3** and that at 24.0 ppm is due to **4**.

The addition of $ThSeCH_2CH_2OPh$ results in the substitution of the PhCN ligands in $[PdCl_2(NCPh)_2]$ and formation of $[PdCl_2\{Se(Th)CH_2CH_2OPh\}_2]$ (**5**), as inferred by the observation of the ^{77}Se resonance at 268 ppm in the NMR spectrum of the reaction solution at this stage {c.f. $\delta(^{77}Se) = 233$ ppm observed for $[PdCl_2(SeMeTh)_2]$ [43]}. The $^{13}C\{^1H\}$ spectrum showed resonances at 36.7 [*1C*; *C*(*n*18)], 63.8 [*1C*; C(*n*17)], 114.7 [*2C*; C(*n*12), C(*n*16)], 120.3 [*1C*; C(*n*14)], 121.4 [*1C*; C(*n*1)], 127.9 [*1C*; C(*n*3)], 129.5 [*2C*; C(*n*13), C(*n*15)], 132.9 [*1C*; C(*n*2)], 136.2 [*1C*; C(*n*4)] and 157.9 ppm [*1C*; C(*n*11)]. They can be interpreted in terms of a $ThSeCH_2CH_2OPh$ ligand coordinated to palladium. The resonance at 36.7 ppm due to C(*n*18) has shifted 7.4 ppm downfield from the corresponding resonance in free **2**. Similar downfield shift of 6 ppm has been observed for the methyl carbon in the case of coordination of ThSeMe to palladium in $[PdCl_2(SeMeTh)_2]$ [43]. The resonance at 120.3 ppm due to the quaternary carbon in the thienyl ring C(*n*1) has shifted 2.4 ppm upfield from the corresponding resonance in **2** in agreement with the upfield shift of 2 ppm observed

Table 2
Selected bond lengths [Å] and angles [°] for *cis*-[$Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeTh)(PPh_3)_2$] (**3**) and *trans*-[$PdCl_2(PPh_3)_2$] (**4**)

cis-[$Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeTh)(PPh_3)_2$] (**3**)				*trans*-[$PdCl_2(PPh_3)_2$] (**4**)7(7)			
Bond lengths		Bond angles		Bond lengths		Bond angles	
Pd(1)–Se(1)	2.4376(7)	Se(1)–Pd(1)–Cl(1)	177.27(3)	Pd(1)–Cl(1)	2.2997(7)	Cl(1)–Pd(1)–P(1)	93.36(2)
Pd(1)–Cl(1)	2.388(1)	Se(1)–Pd(1)–Cl(3)	85.71(4)	Pd(1)–P(1)	2.3247(6)	Cl(1)–Pd(1)–Cl(1) [a]	180.0
Pd(1)–Cl(3)	2.418(1)	Se(1)–Pd(1)–P(1)	92.99(4)			Cl(1)–Pd(1)–P(1) [a]	86.64(2)
Pd(1)–P(1)	2.243(1)	Cl(1)–Pd(1)–Cl(3)	93.52(5)			P(1)–Pd(1)–P(1) [a]	180.0
Pd(2)–Se(1)	2.4092(9)	Cl(1)–Pd(1)–P(1)	87.92(5)				
Pd(2)–Cl(2)	2.346(1)	Cl(3)–Pd(1)–P(1)	176.75(4)				
Pd(2)–Cl(3)	2.450(1)	Se(1)–Pd(2)–Cl(2)	177.89(3)				
Pd(2)–P(2)	2.275(1)	Se(1)–Pd(2)–Cl(3)	85.71(4)				
Se(1)–C(11)	1.936(4)	Se(1)–Pd(2)–P(2)	94.59(4)				
		Cl(2)–Pd(2)–Cl(3)	92.66(5)				
		Cl(2)–Pd(2)–P(2)	87.12(5)				
		Cl(3)–Pd(2)–P(2)	179.74(4)				
		Pd(1)–Se(1)–Pd(2)	94.57(3)				
		Pd(1)–Cl(3)–Pd(2)	94.02(5)				
		Pd(1)–Se(1)–C(11)	100.9(1)				
		Pd(2)–Se(1)–C(11)	99.9(1)				

[a] Symmetry operation: $1-x$, y, $1+z$.

for ThSeMe [43]. Other resonances of **2** are not affected by the coordination.

It is conceivable that upon addition of [$NiCl_2(PPh_3)_2$] into the reaction solution, the PPh_3 ligands substitute one or two $ThSeCH_2CH_2OPh$ ligands in the mononuclear complex **5** resulting in the precipitation of $NiCl_2$ and the formation of *trans*-[$PdCl_2(PPh_3)_2$] (**4**) or [$PdCl_2\{Se(Th)(CH_2CH_2OPh)\}(PPh_3)$] (**6**) depending on the number of substituted ligands. The elimination of $ClCH_2CH_2OPh$ from **6** followed by a fast reaction with another molecule of **6** together with the elimination of $ThSeCH_2CH_2OPh$ may explain the formation of [$Pd_2Cl_2(\mu\text{-}Cl)(\mu SeTh)(PPh_3)_2$] (**3**).

4. Supplementary material

Crystallographic information for compounds **1**–**4** (excluding tables of structure factors) has been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 205516–205519, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Financial support from Academy of Finland is gratefully acknowledged.

References

[1] S.G. Murray, F.R. Hartley, Chem. Rev. 81 (1981) 365.

[2] H.J. Gysling, Coord. Chem. Rev. 42 (1982) 133.

[3] H.J. Gysling, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Selenium and Tellurium Compounds, vol. 1, Wiley, New York, 1986, p. 221.

[4] E.G. Hope, W. Levason, Coord. Chem. Rev. 122 (1993) 171.

[5] W. Levason, S.D. Orchard, G. Reid, Coord. Chem. Rev. 225 (2002) 159.

[6] E.W. Abel, D.G. Evans, J.R. Koe, M.B. Hursthouse, M. Mazid, J. Chem. Soc. Dalton Trans. (1992) 663.

[7] S. Chaudhury, V.K. Jain, R.P. Patel, J. Chem. Res. 486 (1996) 2801.

[8] P.G. Jones, M.C.R. de Arellano, J. Chem. Soc. Dalton Trans. (1996) 2713.

[9] L.P. Wei, F.L. Xiu, S.X. Han, C.H. You, Z.H. Sheng, Chin. J. Chem. 13 (1995) 47.

[10] J.L. Li, J.B. Meng, Y.M. Wang, J.T. Wang, T. Matsuura, J. Chem. Soc. Perkin Trans. 1 (2001) 1140.

[11] C. Bornet, R. Amardeil, P. Meunier, J.C. Daran, J. Chem. Soc. Dalton Trans. (1999) 1039.

[12] M.W. Esterhuysen, R. Brull, H.G. Raubenheimer, C. Esterhuysen, G.J. Kruger, J. Organomet. Chem. 619 (2001) 164.

[13] M.K. Davies, W. Levason, G. Reid, J. Chem. Soc. Dalton Trans. (1996) 2185.

[14] S. Muralidharan, M. Hojjantie, M. Firestone, H. Freiser, J. Org. Chem. 54 (1989) 393.

[15] M.S. Kharasch, R.C. Seyler, F.R. Mayo, J. Am. Chem. Soc. 60 (1938) 882.

[16] L.M. Venanzi, J. Chem. Soc. 719 (1958).

[17] R.C. Burns, M.J. Collins, R.J. Gillespie, G.J. Schrobilgen, Inorg. Chem. 25 (1986) 4465.

[18] G.M. Sheldrick, SHELXS-97. Program for Crystal Structure Determination, University of Göttingen, 1997.

[19] G.M. Sheldrick, SHELXL-97. Program for Crystal Structure Refinement, University of Göttingen, 1997.

[20] A.B. Pomilio, M.C. Tettamanzi, G.P. Romanelli, J.C. Autino, A.A. Vitale, Magn. Reson. Chem. 34 (1965) 165.

[21] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgrén, Z. Naturforsch. 55b (2000) 1.
[22] R.S. Laitinen, R. Oilunkaniemi, M. Ahlgrén, Z. Kristallogr. NCS 216 (2001) 55.
[23] H.C.E. McFarlane, W. McFarlane, J. Chem. Soc. Dalton Trans. (1973) 2416.
[24] D.H. O'Brien, N. Dereu, C.-K. Huang, K.J. Irgolic, F.F. Knapp, Jr., Organometallics 2 (1983) 305.
[25] M. Baiwir, G. Llabrès, A. Luxen, L. Christiaens, J.-L. Piette, Org. Magn. Reson. 22 (1984) 312.
[26] W. Nakanishi, S. Hayashi, H. Tukada, H. Iwamura, J. Phys. Org. Chem. 3 (1990) 358.
[27] M. Taimisto, R.S. Laitinen, R. Oilunkaniemi, M. Ahlgrén, to be submitted.
[28] V.K. Jain, S. Kannan, J. Organomet. Chem. 439 (1992) 231.
[29] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, Polyhedron 14 (1995) 3641.
[30] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, J. Chem. Res. Synopsis, 6 (1996) 284.
[31] S. Dey, V.K. Jain, B. Varghese, J. Organomet. Chem. 623 (2001) 48.
[32] V.K. Jain, R.P. Patel, K.V. Muralidharan, R. Bohra, Polyhedron 8 (1989) 2151.
[33] J.H. Yamamoto, G.P.A. Yap, C.M. Jensen, J. Am. Chem. Soc. 113 (1991) 5060.
[34] E.M. Padilla, J.A. Golen, P.N. Richmann, C.M. Jensen, Polyhedron 10 (1991) 1343.
[35] E.C. Alyea, S. Kannan, G. Ferguson, Acta Crystallogr. C 56C (2000) e493.
[36] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgrén, J. Organomet. Chem. 587 (1999) 200.
[37] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgrén, J. Organomet. Chem. 623 (2001) 168.
[38] G. Ferguson, R. McCrindle, A.J. McAiees, M. Parvez, Acta Crystallogr. Sect. B 38 (1982) 2679.
[39] Y. Kitano, Y. Kinoshita, R. Nakamura, T. Ashida, Acta Crystallogr. Sect. C 39 (1983) 1015.
[40] J.L. Stark, K.H. Whitmire, Acta Crystallogr. Sect. C 53 (1997) 9700007.
[41] S.P. Gubin, L.G. Kuznina, A. Ryabov, A.V. Churakov, Private Communication, Cambridge Crystallographic Data Center (1998) 101524.
[42] J. Vicente, I.M. Saura-Llamas, M.C. Ramirez de Arellano, Private Communication, Cambridge Crystallographic Data Centre (1997) 100454.
[43] R. Oilunkaniemi, J. Komulainen, R.S. Laitinen, M. Ahlgrén, J. Pursiainen, J. Organomet. Chem. 571 (1998) 129.