Formation and structural characterization of novel polynuclear palladium selenolato complexes [Pd3Se(SePh)3(PPh3)3]Cl and [Pd6Cl2Se4(SePh)2(PPh3)6]

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

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

Abstract

In addition to well-known dinuclear phenylselenolato palladium complexes, the reaction of $[PdCl_2(PPh_3)_2]$ and NaSePh affords small amounts of novel trinuclear and hexanuclear complexes $[Pd_3Se(SePh)_3(PPh_3)_3]Cl$ (**1**) and $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6]$ (**2**). Complex **1** is triclinic, $P\bar{1}$, $a = 13.6310(2)$, $b = 16.2596(2)$, $c = 16.9899(3)$ Å, $\alpha = 83.1738(5)$, $\beta = 78.9882(5)$, $\gamma = 78.7635(5)°$. Complex **2** is monoclinic, $C2/c$, $a = 25.7165(9)$, $b = 17.6426(8)$, $c = 27.9151(14)$ Å, $\beta = 110.513(2)°$. There are no structural forerunners for **1**, but the hexanuclear complex **2** is isostructural with $[Pd_6Cl_2Te_4(TeR)_2(PPh_3)_6]$ (R = Ph, C_4H_3S) that have been observed as one of the products in the oxidative addition of R_2Te_2 to $[Pd(PPh_3)_4]$. Mononuclear palladium complexes may play a significant role as building blocks in the formation of the polynuclear complexes.
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1. Introduction

Palladium and platinum form a variety of mono- and polynuclear selenolato and tellurolato complexes (for reviews, see Refs. [1–6]). They can conveniently be prepared by the treatment of halogenated metal complexes with RE^- (E = Se, Te; R = alkyl, aryl) obtained though reduction of R_2E_2 (E = Se, Te) [7–13], or by the oxidative addition of the R_2E_2 to low-valent transition metal centers [10,12,14–16]. The formation of the complexes is a complicated process and the product distribution depends on the choice of chalcogen element, the metal center, organic group, solvent, and the molar ratio of the reagents [14–16].

The most important single factor is the identity of the chalcogen atom. The reactions involving R_2Se_2 mainly result in the formation of mono- or dinuclear complexes [12,14,16], but those involving ditellurides lead to more complicated structures [15,16]. While palladium generally has a tendency towards higher nuclearity than platinum, the existence of stable mononuclear $[PdCl(SePh)(PPh_3)_2]$ has also been reported [16]. On the other hand, Alyea et al. [11] noted a facile decomposition of $[Pd(SePh)_2(PPh_3)_2]$ that apparently resulted in the polymerisation of the complex. When PPh_3 was replaced by less bulky phosphines, it was possible to isolate mononuclear palladium complexes.

Mononuclear chalcogenolato complexes play a significant role as building blocks for polynuclear palladium complexes. It has been suggested [15–19] that they are formed from mononuclear complexes by successive condensation reactions, as shown in Fig. 1. This kind of structural relationship was initially suggested for the formation on hexanuclear $[Pd_6Te_6(PEt_3)_8]$ involving a dinuclear intermediate $[Pd_2Te_4(PEt_3)_4]$ [18], but because $[Pd_6Cl_2Te_4(TeR)_2(PPh_3)_6]$ {R = Ph, C_4H_3S [15,16]} complexes that are obtained though oxidative addition of R_2E_2 to $[Pd(PPh_3)_4]$ contain the same framework as

* Corresponding authors. Fax: +358-8-553-1608.
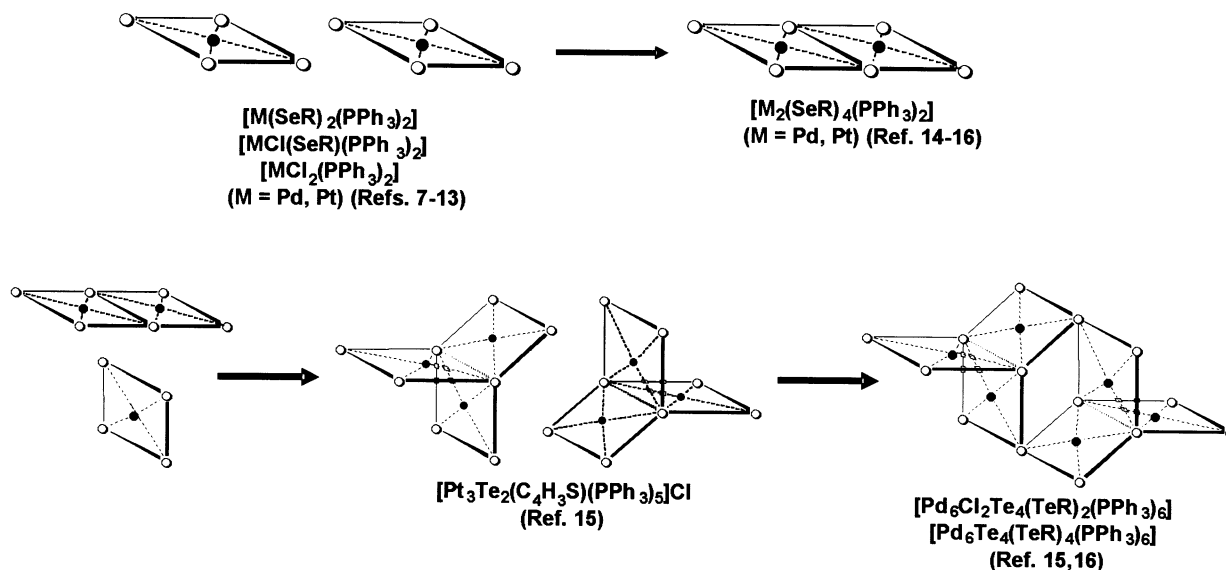*E-mail address:* risto.laitinen@oulu.fi (R.S. Laitinen).

Fig. 1. The structural relationships between the mononuclear, dinuclear, trinuclear, and hexanuclear chalcogenolato complexes suggested by Brennan et al. [18]. Some illustrative examples are cited in the figure.

$[Pd_6Te_6(PEt_3)_8]$, their formation probably goes through similar stages. The suggested formation of $[Pd_2\{Te-(C_4H_3S)\}_4(PPh_3)_2]$ from $(C_4H_3S)_2Te_2$ and $[Pd(PPh_3)_4]$ in benzene [20] lends credibility to this reaction scheme.

In this work we revisit the reaction of $[PdCl_2(PPh_3)_2]$ with $PhSe^-$ as a part of the systematic investigation on the trends in structural and chemical properties of the transition metal complexes with organochalcogen ligands. The main products are dinuclear phenylselenolato palladium complexes [12,14,16]. In addition, two novel polynuclear complexes $[Pd_3Se(SePh)_3(PPh_3)_3]Cl$ and $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6]$ were obtained as side products. While no analogous forerunners have been reported for **1**, the latter complex exhibits a similar polynuclear framework that has previously been observed for hexanuclear tellurolato [15,16] and tellurido [18] complexes of palladium.

2. Experimental

2.1. Preparations

While the complexation reactions were performed under an Ar atmosphere, the end products could be handled in air. $[PdCl_2(PPh_3)_2]$ (Aldrich), Ph_2Se_2 (Fluka Chemika) and $NaBH_4$ (Merck) were used as received. The solvents were degassed with Ar prior use.

The reaction of $PhSe^-$ with $[PdCl_2(PPh_3)_2]$ was explored by using two different molar ratios. The first batch involved the metal-to-ligand molar ratio of 2:1.

The CH_2Cl_2 solution of NaSePh [4 ml, prepared in situ from 0.0283 g (0.09 mmol) of Ph_2Se_2 by reduction with $NaBH_4$] was added to the suspension of $[PdCl_2(PPh_3)_2]$ (0.2541 g, 0.36 mmol) in 14 ml of CH_2Cl_2. The clear reaction mixture was obtained and was stirred overnight at room temperature (r.t.). The solution was concentrated by partial evaporation of CH_2Cl_2. Slow crystallization of the filtered solution afforded a small amount of red crystals of $[Pd_3Se(SePh)_3(PPh_3)_3]Cl\cdot(1/6)CH_2Cl_2$ (**1**) (ca. 5%). Anal. Calc. for $[Pd_3Se(SePh)_3(PPh_3)_3]Cl\cdot(1/6)CH_2Cl_2$: C, 50.89; H, 3.59. Found: C, 51.82; H, 3.79%. $^{31}P\{^1H\}$-NMR (CH_2Cl_2, 298 K): $\delta = 20.6$ ppm.

The second batch involved the metal-to-ligand molar ratio of 1:2. CH_2Cl_2 solution of NaSePh {6 ml, prepared in situ from Ph_2Se_2 (0.0533 g, 0.171 mmol)} was added to the suspension of 0.1187 g (0.169 mmol) $[PdCl_2(PPh_3)_2]$ in 10 ml CH_2Cl_2. The filtered reaction mixture was allowed to stand at r.t. for 2 weeks during which time dark red crystals of $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6]\cdot(5/4)CH_2Cl_2$ (**2**) were separated. The variable amount of the solvent in the crystals precluded accurate elemental analysis.

2.2. $^{31}P\{^1H\}$-NMR spectroscopy

The $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker DPX 400 operating at 161.98 MHz. The spectral width, the pulse width, and the pulse delay were 48.543 kHz, 7.5 μs and 1.0 s, respectively. H_3PO_4 (85%) was used as an external standard. The ^{31}P chemical shifts are

reported relative to the external standard. The spectra of the samples were recorded unlocked.

2.3. X-ray crystallography

Diffraction data for **1** and **2** were collected on a Nonius Kappa CCD diffractometer at 150 K using graphite monochromated $Mo-K_\alpha$ radiation ($\lambda = 0.71073$ Å) by recording 360 frames via φ-rotation ($\Delta\varphi = 1°$; twice 30–60 s per frame). Crystal data and the details of structure determination are given in Table 1.

Table 1
Details of the structure determination of $[Pd_3Se(SePh)_3(PPh_3)_3]Cl\cdot(1/6)CH_2Cl_2$ (**1**) and $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6]\cdot(5/4)CH_2Cl_2$ (**2**)

	1	2
Empirical formula	$C_{72.17}H_{60.33}Cl_{1.33}P_3Pd_3Se_4$	$C_{60.30}H_{50}Cl_{2.10}P_3Pd_3Se_3$
Relative molecular mass	1702.80	1498.04
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	13.6310(2)	25.7165(9)
b (Å)	16.2596(2)	17.6426(8)
c (Å)	16.9899(3)	27.9151(14)
α (°)	83.1738(5)	
β (°)	78.9882(5)	110.513(2)
γ (°)	78.7635(5)	
V (Å^3)	3612.31(9)	11862.2(9)
T (K)	150(2)	150(2)
Z	2	8
$F(000)$	1670	5860
D_{calc} (g cm^{-3})	1.566	1.678
$\mu(Mo-K_\alpha)$ (mm^{-1})	2.908	2.953
Crystal size (mm)	$0.25 \times 0.15 \times 0.10$	$0.15 \times 0.10 \times 0.10$
θ range (°)	1.83–25.00	1.69–25.00
Number of reflections collected	46 057	30 410
Number of unique reflections	11 873	9924
Number of observed reflections [a]	9739	5056
Number of parameters	752	663
R_{int}	0.0568	0.1132
R_1 [b]	0.0543	0.0733
wR_2 [b]	0.1370	0.1448
R_1 (all data)	0.0674	0.1742
wR_2 (all data)	0.1445	0.1822
Goodness-of-fit	1.033	1.053
Max. and min. heights in final difference Fourier synthesis (e Å^{-3})	2.703, −0.605	1.079, −1.087

[a] $I > 2\sigma(I)$.
[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \Sigma wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

The structures were solved by direct methods using SHELXS-97 [21] and refined using SHELXL-97 [22]. 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 = 0.95 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 with the programs.

The solvent CH_2Cl_2 molecules in both **1** and **2** turned out to be severely disordered and the attempts to identify individual atoms and molecules failed. Therefore, the SQUEEZE procedure [23] implemented in PLATON software [24,25] was utilized to obtain a new set of $F^2(hkl)$ values from which the contribution of the solvent molecules was removed. The potential solvent accessible volumes in the unit cells of **1** and **2** were 477.1 and 1721.8 Å^3, respectively, corresponding to the respective volumes in the asymmetric units of 238.5 and 215.2 Å^3. The respective estimated electron counts were 14 and 213 electrons/unit cell, corresponding to the approximate formulae of $\mathbf{1}\cdot(1/6)CH_2Cl_2$ and $\mathbf{2}\cdot(5/4)CH_2Cl_2$.

3. Results and discussion

3.1. The reaction of $[PdCl_2(PPh_3)_2]$ and $PhSe^-$

The treatment of $[PtCl_2(PPh_3)_2]$ with $PhSe^-$ generally affords isomers of mononuclear $[Pt(SePh)_2(PPh_3)_2]$ [7,8,10]. While the reaction of $[PdCl_2(L)_2]$ with $PhSe^-$ also produces mononuclear $[Pd(SePh)_2(L)_2]$ (L = PMe_3, PEt_3, $P(n-Bu)_3$, $PMePh_2$) [11], that involving $[PdCl_2(PPh_3)_2]$ results in the formation of dinuclear, polynuclear, and even polymeric species depending on the molar ratios of the elements [11,12]. The oxidative addition of R_2Se_2 to $[Pd(PPh_3)_4]$ also produces mainly dinuclear selenolatopalladium complexes [11,12,14,16].

In addition to the dinuclear main products, the 2:1 reaction of $[PdCl_2(PPh_3)_2]$ and $PhSe^-$ also affords small amounts of trinuclear $[Pd_3Se(SePh)_3(PPh_3)_3]Cl\cdot(1/6)CH_2Cl_2$ (**1**). In case of the metal-to-ligand molar ratio of 1:2, hexanuclear $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6]\cdot(5/4)CH_2Cl_2$ (**2**) is obtained. The redissolved crystals of the former complex exhibited the $^{31}P\{^1H\}$ resonance of 20.6 ppm. The $^{31}P\{^1H\}$-NMR spectrum of **2** is complicated, indicating the presence of several different species in the solution. It is interesting to note that while the assignment of the complicated $^{31}P\{^1H\}$ spectrum of **2** was not possible, its overall appearance was very similar to that observed for the tellurium analogues of **2**, $[Pd_6X_2Te_4(TeR)_2(PPh_3)_6]\cdot nCH_2Cl_2$

(X = Cl, C₄H₃STe⁻; R = Ph, C₄H₃S) [15,16]. This indicates that the hexanuclear complex may only exist in the solid state.

3.2. Crystal structures

The molecular structure and the numbering of the atoms of [Pd₃Se(SePh)₃(PPh₃)]Cl·(1/6)CH₂Cl₂ (**1**) are shown in Fig. 2. Selected bond lengths and angles are listed in Table 2.

Complex **1** is composed of discrete trinuclear cations and chloride anions. Each palladium atom in the cation shows approximate square-planar coordination [the sums of the four bond angles around palladium atoms Pd(1), Pd(2), and Pd(3) are 360.89, 359.32 and 360.71°, respectively; see Table 2] and is bridged to two other palladium atoms by phenylselenolato ligands. The Pd₃Se₄ framework is completed by a capping μ_3-Se^{2-} ligand linking all palladium atoms together, as shown in Fig. 2. The cation bears no structural relationship with any known polynuclear palladium or platinum chalcogen complex, though a similar Pd₃(μ_3-E) (E = Se or Te) subunit has been observed in [Pd₃Se₂(SeSiMe₃)₂(PPh₃)₄] [26], [Pt₃Te₂(Th)(PPh₃)₅]Cl and [Pd₆Cl₂Te₄(TeR)₂-(PPh₃)₆]·2CH₂Cl₂ [15,16].

The lengths of the Pd–Se bonds involving the bridging PhSe⁻ ligand [2.4462(8)–2.4680(8) Å] and those involving the μ_3-Se ligand [2.4477(8)–2.4632(8) Å] are virtually identical and close to single bond lengths (the sum of the covalent radii of palladium and selenium is 2.45 Å [27]). In [Pd₃Se₂(SeSiMe₃)₂(PPh₃)₄], the bonds involving the μ_2-⁻SeR ligands are longer [2.482(3)–

2.499(3) Å] than those involving μ_3-Se^{2-} [2.434–2.467(3) Å] [26]. The Pd–P bond lengths span a range of 2.304(2)–2.312(2) Å in agreement with those in [Pd₃Se₂(SeSiMe₃)₂(PPh₃)₄] [2.288(9)–2.345(9) Å] [26]. The chloride anions and the solvent molecules in **1** are disordered between the layers of the cations.

The molecular structure and the numbering of the atoms of [Pd₆Cl₂Se₄(SePh)₂(PPh₃)₆]·(5/4)CH₂Cl₂ (**2**) are shown in Fig. 3. The selected bond lengths and angles are listed in Table 3. Complex **2** is isomorphic and

Table 2
Selected bond lengths (Å) and angles (°) of [Pd₃Se(SePh)₃(PPh₃)₃]Cl·(1/6)CH₂Cl₂ (**1**)

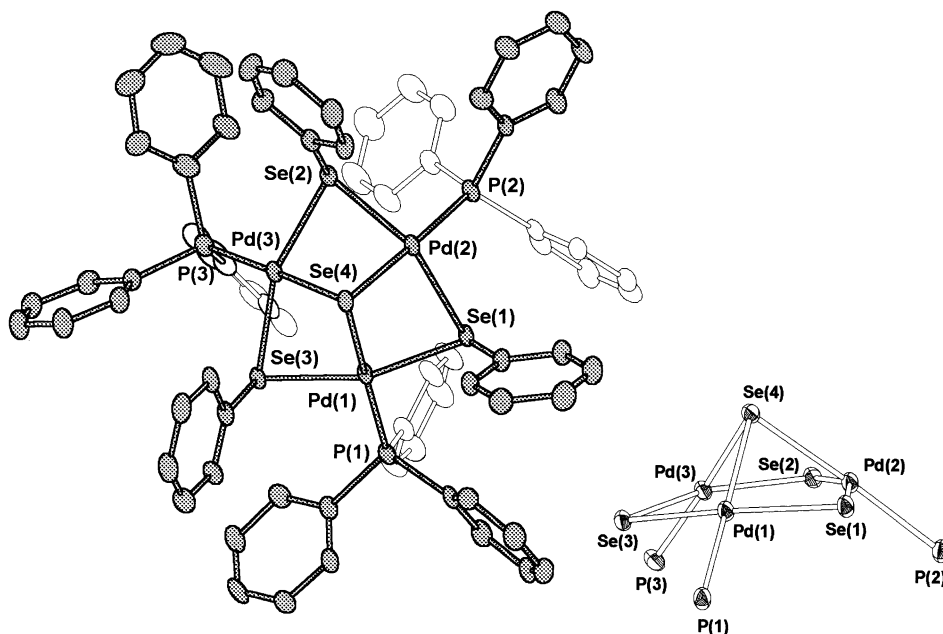| Bond lengths			
Pd(1)–P(1)	2.304(2)	Pd(2)–Se(2)	2.4488(8)
Pd(1)–Se(1)	2.4462(8)	Pd(2)–Se(4)	2.4477(8)
Pd(1)–Se(3)	2.4573(8)	Pd(3)–P(3)	2.305(2)
Pd(1)–Se(4)	2.4632(8)	Pd(3)–Se(2)	2.4680(8)
Pd(2)–P(2)	2.312(2)	Pd(3)–Se(3)	2.4501(8)
Pd(2)–Se(1)	2.4584(8)	Pd(3)–Se(4)	2.4485(8)
Bond angles			
P(1)–Pd(1)–Se(1)	95.38(5)	P(3)–Pd(3)–Se(2)	97.26(5)
P(1)–Pd(1)–Se(3)	96.31(5)	P(3)–Pd(3)–Se(3)	93.65(5)
P(1)–Pd(1)–Se(4)	176.89(5)	P(3)–Pd(3)–Se(4)	177.53(5)
Se(1)–Pd(1)–Se(3)	159.41(3)	Se(2)–Pd(3)–Se(3)	158.54(3)
Se(1)–Pd(1)–Se(4)	84.13(3)	Se(2)–Pd(3)–Se(4)	84.26(3)
Se(3)–Pd(1)–Se(4)	85.07(2)	Se(3)–Pd(3)–Se(4)	85.54(3)
P(2)–Pd(2)–Se(1)	97.48(5)	Pd(1)–Se(1)–Pd(2)	80.22(2)
P(2)–Pd(2)–Se(2)	92.96(5)	Pd(2)–Se(2)–Pd(3)	80.20(2)
P(2)–Pd(2)–Se(4)	177.07(5)	Pd(1)–Se(3)–Pd(3)	79.77(2)
Se(1)–Pd(2)–Se(2)	158.52(3)	Pd(1)–Se(4)–Pd(2)	80.10(2)
Se(1)–Pd(2)–Se(4)	84.20(3)	Pd(1)–Se(4)–Pd(3)	79.68(2)
Se(2)–Pd(2)–Se(4)	84.68(3)	Pd(2)–Se(4)–Pd(3)	80.61(2)

Fig. 2. The structure of the cation of [Pd₃Se(SePh)₃(PPh₃)₃]Cl·(1/6)CH₂Cl₂ indicating the numbering of the atoms. The hydrogen atoms have been omitted for clarity. The thermal ellipsoids have been drawn at 50% probability level.
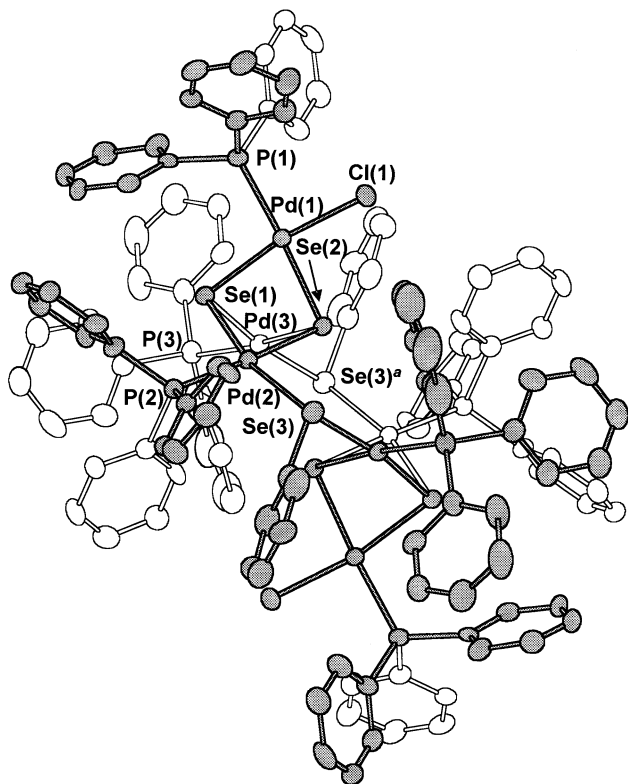
Fig. 3. The molecular structure of $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6]\cdot(5/4)CH_2Cl_2$ indicating the numbering of the atoms. The hydrogen atoms and disordered solvent molecules have been omitted for clarity. The thermal ellipsoids have been drawn at 50% probability level. The superscript a denotes the symmetry operation $-x+1/2$, $-y+1/2$, $-z+1$.

isostructural with $[Pd_6Cl_2Te_4(TeR)_2(PPh_3)_6]$ (R = Ph, C_4H_3S) [15,16]. It also shows the same hexanuclear framework of palladium and chalcogen atoms as $[Pd_6Te_4(TeTh)_4(PPh_3)_2]$ [15] and $[Pd_6Te_6(PEt_3)_8]$ [18]. The structure of **2** is composed of two Pd_3Se_2 fragments joined together into a cyclic hexanuclear complex by two bridging PhSe$^-$ ligands. The Pd_3Se_2 framework has also been reported for a series of palladium complexes [26,28,29].
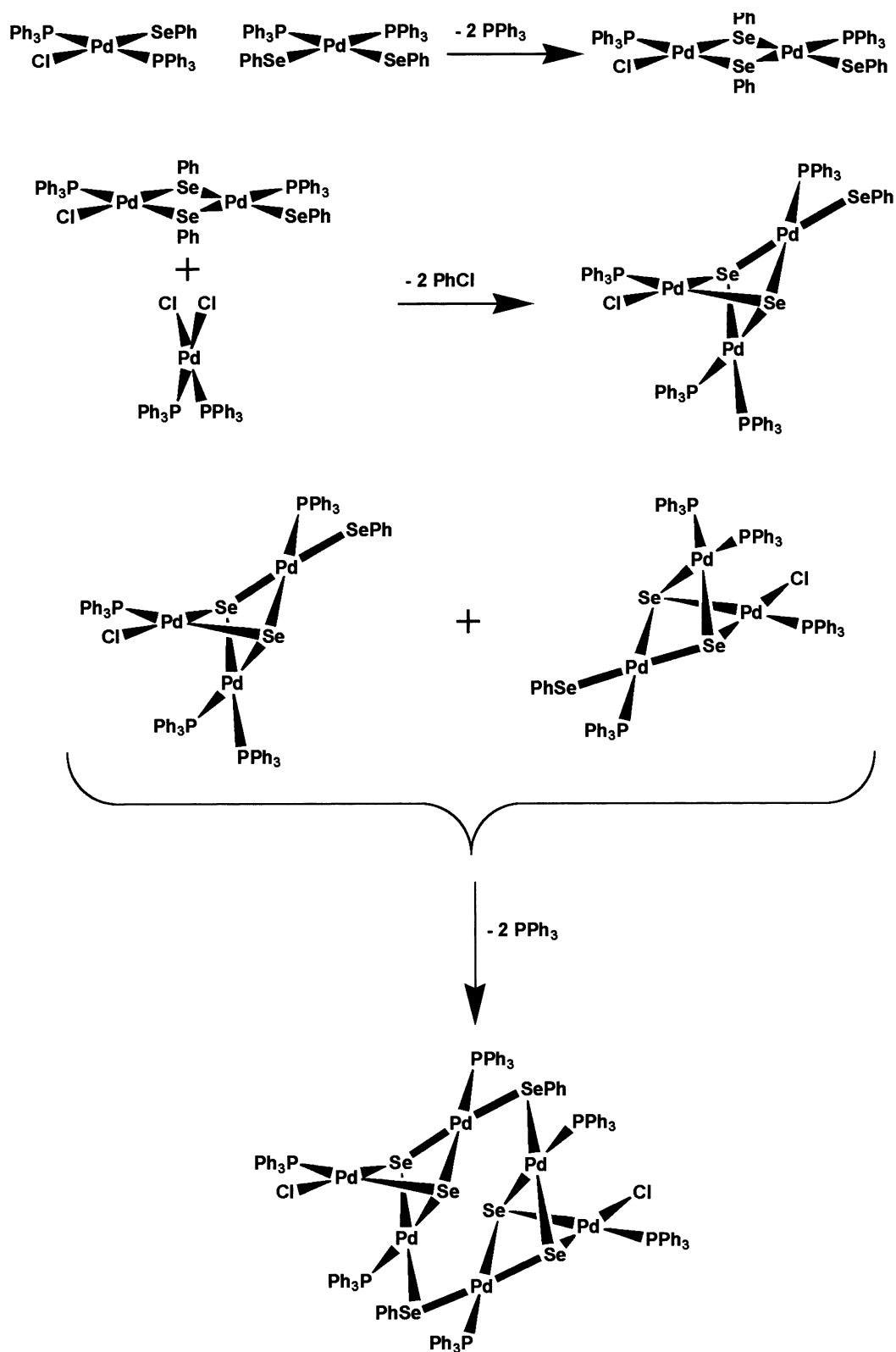
The palladium atoms in **2** also show slightly distorted square-planar coordination [the sums of the four bond angles around palladium atoms Pd(1), Pd(2), and Pd(3) are 360.0, 360.07 and 359.87° respectively; see Table 3]. The Pd–(μ_3-Se) bond lengths span a range of 2.410(2)–2.456(2) Å (average 2.4311 Å) and the Pd–(μ_2-Se) bond lengths are 2.453(2) and 2.454(2) Å. The Pd–Se bonds in **2** are quite normal and can be compared to those in **1**. The Pd–Cl bond length of 2.365(3) Å and the Pd–P bond lengths of 2.285(3)–2.291(3) Å also indicate normal single bonds.

The CH_2Cl_2 solvent molecules are disordered between the palladium complexes, as expected on the basis of the isomorphic tellurium analogues $[Pd_6X_2Te_4(TeR)_2(PPh_3)_6]\cdot nCH_2Cl_2$ [15,16].

3.3. Formation pathway of polynuclear complexes

While the end products in the reaction between $[PdCl_2(PPh_3)_2]$ and PhSe$^-$ are dinuclear and polynuclear complexes [11,12], the ligand substitution can conceivably produce mononuclear chalcogenolato complexes at least as transient intermediates. The initial reaction mixture may therefore contain *cis*- and *trans*-isomers of $[Pd(SePh)_2(PPh_3)_2]$ (c.f. the reaction of $[PtCl_2(PPh_3)_2]$ and PhSe$^-$ in which these isomers can be isolated [7,8,12]), $[PdCl(SePh)(PPh_3)_2]$ (isolated in the reaction of Ph_2Se_2 and $[Pd(PPh_3)_4]$ in CH_2Cl_2 [16]), unreacted *cis*- and *trans*-$[PdCl_2(PPh_3)_2]$, and even $[PdCl(R)(PPh_3)_2]$ that indicates the cleavage of the Se–C bond (c.f. the formation of $[PdCl(C_4H_3S)(PPh_3)_2]$ through the oxidative addition of $(C_4H_3S)_2Se_2$ to $[Pd(PPh_3)_4]$ in CH_2Cl_2 [14]).

The condensation of various combinations of mononuclear building blocks can be conceived to afford different dinuclear complexes. For instance, the formation of *cis*- and *trans*-isomers of $[Pd_2(SePh)_4(PPh_3)_2]$ can be observed in the $^{31}P\{^1H\}$ spectrum of the reaction mixture ($\delta = 28.9$ and 27.9 ppm [16]). The *trans*-isomer has been isolated and structurally characterized in the oxidative addition of Ph_2Se_2 to $[Pd(PPh_3)_4]$. The application of the structural relationships of Brennan et al. [18] leads to a series of similar condensation steps that rationalize the formation of $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_2]$. This is exemplified by one of the possible pathways in Scheme 1.

Table 3
Selected bond lengths (Å) and angles (°) of $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6]\cdot(5/4)CH_2Cl_2$ (**2**)

Bond lengths			
Pd(1)–P(1)	2.291(3)	Pd(2)–Se(2)	2.4388(16)
Pd(1)–Cl(1)	2.365(3)	Pd(2)–Se(3)	2.4536(16)
Pd(1)–Se(1)	2.4104(15)	Pd(3)–P(3)	2.285(3)
Pd(1)–Se(2)	2.4247(15)	Pd(3)–Se(1)	2.4205(16)
Pd(2)–P(2)	2.286(3)	Pd(3)–Se(3)	2.4526(17)
Pd(2)–Se(1)	2.4365(15)	Pd(3)–Se(2)	2.4559(15)

Bond angles			
P(1)–Pd(1)–Cl(1)	92.30(12)	P(3)–Pd(3)–Se(3)	91.57(11)
P(1)–Pd(1)–Se(1)	97.83(9)	P(3)–Pd(3)–Se(2)	173.12(11)
P(1)–Pd(1)–Se(2)	175.49(10)	Se(1)–Pd(3)–Se(3)^a	171.11(6)
Cl(1)–Pd(1)–Se(1)	169.87(10)	Se(1)–Pd(3)–Se(2)	77.43(5)
Cl(1)–Pd(1)–Se(2)	91.65(10)	Se(2)–Pd(3)–Se(3)^a	95.07(5)
Se(1)–Pd(1)–Se(2)	78.22(5)	Pd(1)–Se(1)–Pd(2)	89.82(5)
P(2)–Pd(2)–Se(1)	98.59(9)	Pd(1)–Se(1)–Pd(3)	83.89(5)
P(2)–Pd(2)–Se(2)	175.75(10)	Pd(3)–Se(1)–Pd(2)	81.37(5)
P(2)–Pd(2)–Se(3)	96.28(10)	Pd(1)–Se(2)–Pd(3)	82.85(5)
Se(1)–Pd(2)–Se(2)	77.45(5)	Pd(1)–Se(2)–Pd(2)	89.43(5)
Se(1)–Pd(2)–Se(3)	164.82(6)	Pd(2)–Se(2)–Pd(3)	80.61(5)
Se(2)–Pd(2)–Se(3)	87.75(5)	Pd(2)–Se(3)–Pd(3)^a	109.27(6)

^{a} Symmetry operation: $-x+1/2$, $-y+1/2$, $-z+1$.

Scheme 1.

The formation of [Pd$_3$Se(SePh)$_3$(PPh$_3$)$_3$]Cl (**1**) from mononuclear complexes can be explained by a slightly modified scheme (see Scheme 2). The second condensation step involving a third mononuclear complex results in the sharing of three edges between the dinuclear and mononuclear complexes.
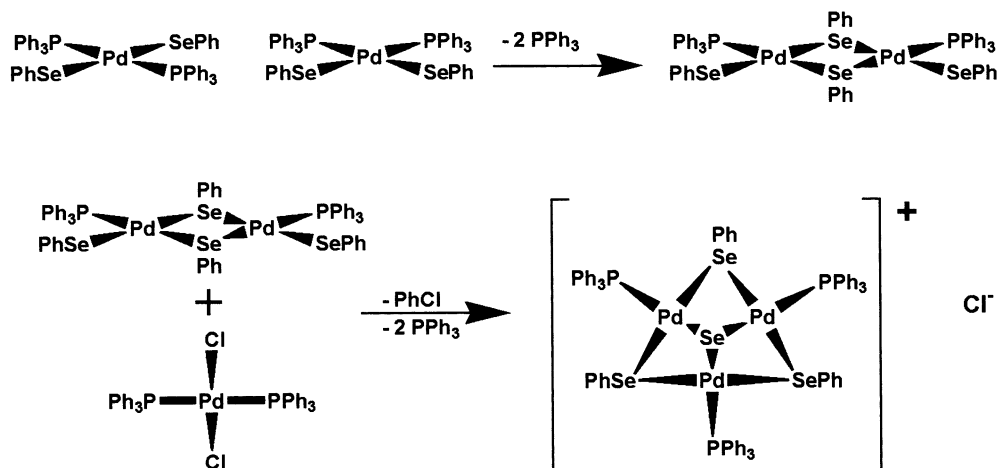
Scheme 2.

4. Supplementary material

Crystallographic information for complexes **1** and **2** (excluding tables of structure factors) has been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 216762 and 216763, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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