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The oxidative addition of diphenyl diselenide and ditelluride to tetrakis(triphenylphosphine)palladium

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Abstract

The oxidative addition of diphenyl diselenide to $[Pd(PPh_3)_4]$ in dichloromethane results in the formation of a dinuclear complex $[Pd_2(SePh)_4(PPh_3)_2]$ (**1**) and a mononuclear complex $[PdCl(SePh)(PPh_3)_2]$ (**2**) that have been identified and characterized structurally by X-ray crystallography and ^{31}P-NMR spectroscopy. The analogous reaction involving diphenyl ditelluride leads to a mixture of products. $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]\cdot 1/2CH_2Cl_2$ (**3**) can be isolated and its X-ray structure determined. While the oxidative addition of Ph_2Se_2 mainly involves the clevage of the Se–Se bond, that of Ph_2Te_2 indicates the rupture of both Te–Te and C–Te. Cumulative evidence shows that the choice of the central atom and the solvent also plays an important role in the oxidative addition. The final polynuclear complexes can be conceived to be formed from the mononuclear addition products by sequential condensation steps. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aromatic diselenides; Aromatic ditellurides; Palladium complexes; X-ray crystallography; NMR spectroscopy

1. Introduction

The coordination chemistry of transition metal complexes with organoselenide and telluride ligands is a rapidly developing area of organometallic chemistry [1–4]. They may provide a low-temperature route for binary transition metal selenides and tellurides, such as PdTe and NiTe [5–7] that find potential applications in materials science. One way to prepare chalcogenolato complexes involves the oxidative addition of diorganodichalcogenides to low-valent transition metal centers that often results in the cleavage of the chalcogen–chalcogen bond and the formation of mono- or dinuclear complexes with anionic bridging or terminal RE^- ligands [3]. In some cases the addition of diaryl dichalcogenides to zerovalent Group 10 metals has been found to lead to the cleavage of the carbon–chalcogen bond [8–14]. The oxidative addition of organochalcogen compounds to low-valent transition metal centers may also be an initial step in homogeneous catalysis [15].

This paper is a part of a systematic investigation of the factors affecting the pathways of oxidative addition of aromatic dichalcogenides to zerovalent palladium and platinum centers. The reaction pathway depends on the chemical identity of both the chalcogen atom and the Group 10 metal. Whereas dithienyl diselenide adds to $[M(PPh_3)_4]$ mainly with the cleavage of Se–Se bond forming mononuclear (M = Pt) or dinuclear (M = Pd, Pt) complexes [12], the reaction of dithienyl ditelluride involves the cleavage of both C–Te and Te–Te bonds [13,14] resulting in the formation of complexes with more complicated structures. The choice of solvent also seems to affect the reaction pathway.

We report the reaction of diphenyl diselenide and ditelluride with tetrakis(triphenylphosphine)palladium in dichloromethane in order to explore the effect of the aromatic group on the oxidative addition[1]. The main products are identified by NMR spectroscopy and structurally characterized by X-ray crystallography.

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[1] The formation of dinuclear $[Pd_2(SePh)_4(PPh_3)_2]$ from Ph_2Se_2 and $[Pd(PPh_3)_4]$ in benzene has been reported, but no structural information has been given [16].

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2. Experimental

2.1. General

Synthetic work was carried out under a dry argon atmosphere. Dichloromethane was distilled on CaH_2 and purged with argon before use. Tetrakis-(triphenylphosphine)palladium $[Pd(PPh_3)_4]$, diphenyl diselenide Ph_2Se_2, and diphenyl ditelluride Ph_2Te_2 (Aldrich) were used as supplied.

2.2. The reaction of $[Pd(PPh_3)_4]$ with Ph_2Se_2

Ph_2Se_2 (0.064 g, 0.21 mmol) was dissolved in 5 ml of dichloromethane, added into 20 ml of a dichloromethane solution of $[Pd(PPh_3)_4]$ (0.237 g, 0.21 mmol), and stirred overnight. The solution was concentrated by the partial evaporation of dichloromethane. Upon addition of hexane a red precipitate was formed. The precipitate was filtered off, washed with hexane, and dried. The recrystallization from dichloromethane afforded red, tabular crystals of $[Pd_2(SePh)_4(PPh_3)_2]$ (**1**). Yield 0.105 g (75%). Anal. Calc. for $C_{60}H_{50}P_2Pd_2Se_4$: C 52.93, H 3.70; Found: C 52.76, H 3.39.

Upon a slow evaporation of the filtrate a few violet crystals of $[PdCl(SePh)(PPh_3)_2]$ (**2**) were formed.

2.3. The reaction of $[Pd(PPh_3)_4]$ with Ph_2Te_2

The reaction of Ph_2Te_2 (0.075 g, 0.18 mmol) and $[Pd(PPh_3)_4]$ (0.205 g, 0.18 mmol) was carried out in dichloromethane as described above. The reaction mixture was allowed to stand at room temperature for a week. During this time dark black–red crystals of $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]\cdot 1/2CH_2Cl_2$ (**3**) (ca. 0.019 g; 20%) were obtained. The variable, nonstoichiometric amount of solvent in the crystals of the product precluded accurate elemental analysis.

2.4. NMR spectroscopy

The $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker DPX400 spectrometer operating at 161.98 MHz. The spectral width was 58.480 kHz and the pulse width 8.55 μs corresponding to the nuclear tip angle of ca. 45°. The pulse delay was 1.0 s. The accumulations contained ca. 5000–10000 transients. *d*-Chloroform was used as an internal ^2H lock and orthophosphoric acid (85%) as an external standard. The ^{31}P chemical shifts are reported relative to the external standard.

2.5. X-ray crystallography

Diffraction data for **1**–**3** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) by recording 360 frames via φ-rotation ($\Delta\varphi = 1°$; two times 20–60 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 [17] and refined using SHELXL-97 [18]. 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 to that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated with the programs. Fractional coordinates of all atoms, anisotropic thermal parameters, and the full listing of bond parameters are available as supplementary material as CIF files.

3. Results

3.1. General

The reaction of diphenyl diselenide and $[Pd(PPh_3)_4]$ in dichloromethane affords $[Pd_2(SePh)_4(PPh_3)_2]$ (**1**) with good yields. $[PdCl(SePh)(PPh_3)_2]$ (**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 $[Pd_2(SePh)_4(PPh_3)_2]$ and $[PdCl(SePh)(PPh_3)_2]$ crystallize from dichloromethane or chloroform to yield X-ray quality single crystals.

The oxidative addition of diphenyl ditelluride to $[Pd(PPh_3)_4]$ is similar to that of thienyl ditelluride [13] and affords several products. Hexanuclear, air-stable $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]\cdot 1/2CH_2Cl_2$ (**3**) complexes could be isolated among other, yet unidentified species.

3.2. Crystal structures of $[Pd_2(SePh)_4(PPh_3)_2]$, $[PdCl(SePh)(PPh_3)_2]$, and $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]$

The molecular structures and the numbering of the atoms of *trans*-$[Pd_2(SePh)_4(PPh_3)_2]$ (**1**) and the mononuclear side product *trans*-$[PdCl(SePh)(PPh_3)_2]$ (**2**) are shown in Figs. 1 and 2. Those of $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]\cdot 1/2CH_2Cl_2$ (**3**) are shown in Fig. 3. The selected bond distances and angles are listed in Tables 2 and 3.

All species **1**–**3** form discrete complexes. The dinuclear complex **1** shows a similar molecular structure to *trans*-$[Pd_2(SeTh)_4(PPh_3)_2]$ and *trans*-$[Pt_2(SeTh)_4(PPh_3)_2]$ (Th = thienyl, C_4H_3S) [12], as well as to *trans*-$[Pt_2(SePh)_4(PPh_3)_2]$ [19] with which it is isostructural.

The palladium atoms in all complexes **1**–**3** show expectedly a slightly distorted square-planar coordination geometry (for the individual bond parameters in

Table 1
Details of the structure determination of $[Pd_2(SePh)_4(PPh_3)_2]$ (**1**), $[PdCl(SePh)(PPh_3)_2]$ (**2**) and $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]$ (**3**)

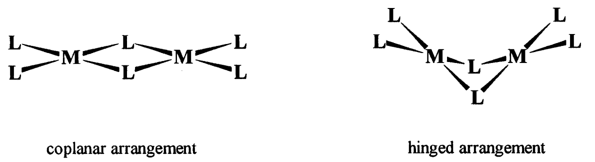
	1	**2**	$\mathbf{3}\cdot 1/2CH_2Cl_2$
Empirical formula	$C_{30}H_{25}PPdSe_2$	$C_{42}H_{35}ClP_2PdSe$	$C_{60.25}H_{50.50}Cl_{1.50}P_3Te_3Pd_3$
Relative molecular mass	680.79	822.45	1622.59
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$C2/c$
a (Å)	28.014(6)	17.533(4)	22.820(5)
b (Å)	9.545(2)	10.900(2)	22.176(4)
c (Å)	22.570(3)	19.832(4)	23.912(5)
β (°)	118.43(3)	109.32(3)	104.98(3)
V (Å^3)	5307.4(5)	3576.8(1)	11690(4)
T (K)	293	120	293
Z	8	4	8
$F(000)$	2672	2176	6212
D_{calc} (g cm^{-3})	1.704	1.527	1.844
μ(Mo–K$_\alpha$) (mm^{-1})	3.520	1.730	2.569
Crystal size (mm)	$0.20\times0.15\times0.10$	$0.25\times0.15\times0.15$	$0.30\times0.15\times0.10$
Theta range (°)	2.80–24.92	2.12–27.49	2.55–23.50
Number of reflections collected	19 085	40 542	15 395
Number of unique reflections	4569	7924	8558
Number of observed reflections [a]	3237	5911	4075
Number of parameters	307	425	638
R_{int}	0.1550	0.0655	0.1291
R_1 [b]	0.0742	0.0342	0.0735
wR_2 [b]	0.1425	0.0666	0.0975
R_1 (all data)	0.1139	0.0584	0.1893
wR_2 (all data)	0.1586	0.0729	0.1234
GOF	0.476	1.077	0.995
Max. and min. heights in final difference Fourier synthesis (e Å^{-3})	0.448, −0.634	0.449, −0.632	0.837, −0.631

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

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

the coordination sphere, see Tables 2 and 3). The sums of the four bond angles around the metal atom are 360.1, 359.2 and 360.1–360.2° for **1**–**3**, respectively, well in accord with the virtually planar coordination. The respective rms deviations of the metal atom and four donor atoms from the coordination planes are 0.0737, 0.0339 and 0.0586–0.0841 for **1**–**3**, respectively.

The two square-planar coordination spheres in dinuclear Pd(II) and Pt(II) complexes can adopt either coplanar or hinged arrangement [3]:



coplanar arrangement hinged arrangement

1 exhibits the coplanar arrangement (see Fig. 1) that seems to be a more common feature in dinuclear palladium or platinum centers involving bridging chalcogen donors than the hinged arrangement [12,13,20–23]. It should be noted, however, that the hinged arrangement is also known for these types of complexes, as exemplified by $[Pd_2\{Se_2C_8H_{12}\}_2(PPh_3)_2]$ [24] and $[Pd_2Cl_2(SeMe)_2\{SeMe(C_4H_2O)\}_2CMe_2\}]$ [25] that show a hinged arrangement in the Pd{μ-SeR}$_2$Pd fragment with the respective angles of 104.4 and 124.5° between the two neighbouring coordination planes.

The bridging phenylselenolato ligands in **1** are not equidistant from the two palladium atoms. The two

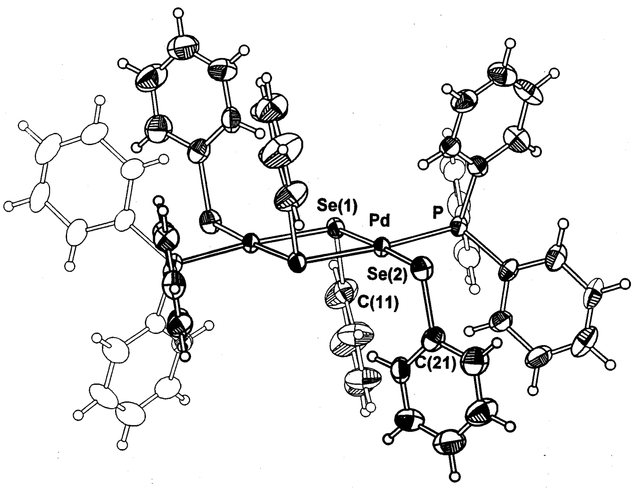


Fig. 1. The molecular structure of $[Pd_2(SePh)_4(PPh_3)_2]$ (**1**) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 30% probability.

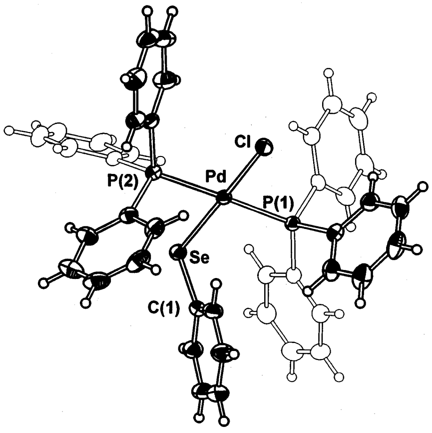


Fig. 2. The molecular structure of [PdCl(SePh)$(PPh_3)_2$] (**2**). The thermal ellipsoids have been drawn at 30% probability.

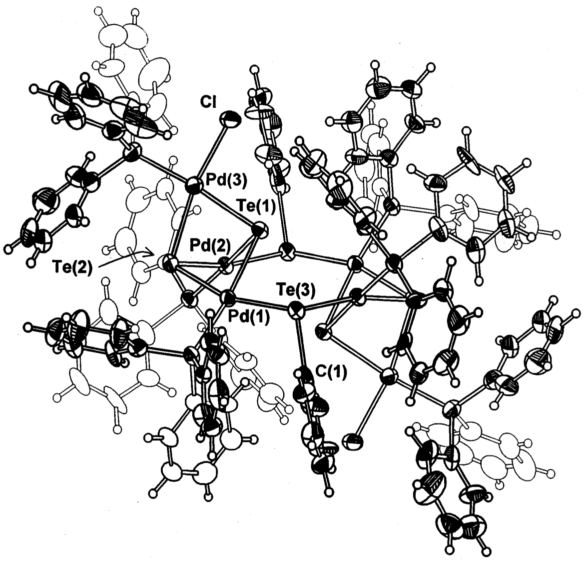
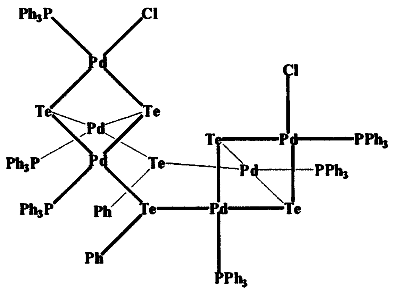


Fig. 3. $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]\cdot 1/2CH_2Cl_2$ (**3**) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 30% probability.

Pd–Se(1) distances are 2.463(1) and 2.494(1) Å (see Table 2). The terminal Pd–Se(2) bond in **1** shows a length of 2.461(1) Å. All these values are close to single bond lengths {the sum of the covalent radii of palladium and selenium is 2.45 Å [26]}. The bridging Pd–Se bonds in $[Pd_2\{Se_2C_8H_{12}\}_2(PPh_3)_2]$ are shorter than those in **1**, but exhibit similar asymmetry (2.413–2.419 and 2.481–2.489 Å) [24] each selenium being closer to the palladium atom to which it is chelating. The terminal Pd–Se distances (2.382–2.387 Å) in $[Pd_2\{Se_2C_8H_{12}\}_2(PPh_3)_2]$ are also shorter than in **1**. In contrast, the Pd(μ–SeR)$_2$Pd unit in $[Pd_2(SeTh)_4(PPh_3)_2]$ is symmetric with all bridging and terminal bonds showing virtually equal lengths [2.466(1) and 2.461(1) Å, respectively] [12]. $[Pd_2Cl_2(SeMe)_2\{SeCH_3(C_4H_2O)\}_2CMe_2\}]$ is also symmetric, the bridging Pd–Se distances spanning a narrow range of 2.396–2.420 Å [25]. The shorter bridging Pd–Se bonds in $[Pd_2\{Se_2C_8H_{12}\}_2(PPh_3)_2]$ [23] and $[Pd_2Cl_2(SeMe)_2\{SeCH_3(C_4H_2O)\}_2CMe_2\}]$ as compared to those in **1** are probably due to the hinged arrangement of the two square-planar coordination planes of the neighbouring palladium atoms, since the lone-pair repulsions between the two selenium atoms are likely to be smaller than in the case of coplanar arrangement (see Fig. 4).

The mononuclear [PdCl(SePh)$(PPh_3)_2$] (**2**) shows a Pd–Se bond length of 2.4200(6) Å. It falls within the range 2.401–2.560 Å of Pd–Se distances observed in mononuclear palladium complexes [27–30]. The differences in the bond lengths can be attributed to the relative effects of the *trans*-influence. The Pd–Se bonds in hexacoordinated palladium complexes containing $PhSe^-$ ligands are exemplified by 2.479–2.506 Å reported for a series of *trans*-$[PdMe_2(SePh)_2L_2]$ (L = Me or $L_2 = H_2CCH_2CH_2CH_2$) complexes [31].

The hexanuclear complex $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]$ (**3**) has a similar structure to $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ and $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ [13]. It is in fact isostruc-



3

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Pd_2(SePh)_4(PPh_3)_2]$ (**1**) and [PdCl(SePh)$(PPh_3)_2$] (**2**)

$[Pd_2(SePh)_4(PPh_3)_2]$ (**1**)		[PdCl(SePh)$(PPh_3)_2$] (**2**)	
Bond lengths			
Pd–P	2.284(2)	Pd–P(1)	2.3485(9)
Pd–Se(1)	2.463(1)	Pd–P(2)	2.3130(9)
Pd–Se(2)	2.461(1)	Pd–Se	2.4200(6)
Pd–Se(1) [a]	2.494(1)	Pd–Cl	2.3468(9)
Se(1)–C(11)	1.925(10)		
Se(2)–C(21)	1.919(11)		
Bond angles			
P–Pd–Se(1)	96.24(7)	P(1)–Pd–P(2)	175.91(3)
P–Pd–Se(2)	87.90(7)	P(1)–Pd–Se	94.23(3)
P–Pd–Se(1) [a]	174.69(4)	P(2)–Pd–Se	82.61(3)
Se(1)–Pd–Se(2)	175.85(4)	P(1)–Pd–Cl	89.71(3)
Se(1)–Pd–Se(1) [a]	84.11(4)	P(2)–Pd–Cl	93.69(3)
Se(2)–Pd–Se(1) [a]	91.80(4)	Se–Pd–Cl	173.36(2)
Pd–Se(1)–Pd(1) [a]	95.89(4)		
C(11)–Se(1)–Pd	98.7(3)		
C(11)–Se(1)–Pd [a]	97.5(3)		
C(21)–Se(2)–Pd	101.8(3)		

[a] Symmetry operation $-x$, $2-y$, $-z$.

Table 3
Selected bond lengths (Å) and bond angles (°) in $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]$ (**3**)

Bond lengths			
Te(1)–Pd(3)	2.591(2)	Te(3)–Pd(2) [a]	2.629(2)
Te(1)–Pd(1)	2.603(1)	Te(3)–Pd(1)	2.647(2)
Te(1)–Pd(2)	2.600(1)	Pd(1)–P(1)	2.310(4)
Te(1)–Te(2)	3.164(1)	Pd(2)–P(2)	2.302(4)
Te(2)–Pd(3)	2.560(1)	Pd(2)–Te(3) [a]	2.629(2)
Te(2)–Pd(1)	2.597(2)	Pd(3)–P(3)	2.311(4)
Te(2)–Pd(2)	2.602(2)	Pd(3)–Cl(1)	2.422(4)
Te(3)–C(1)	2.154(2)		
Bond angles			
Pd(3)–Te(1)–Pd(1)	85.28(5)	Te(2)–Pd(1)–Te(1)	74.95(5)
Pd(3)–Te(1)–Pd(2)	92.20(5)	P(1)–Pd(1)–Te(3)	92.5(1)
Pd(1)–Te(1)–Pd(2)	80.89(4)	Te(2)–Pd(1)–Te(3)	167.47(5)
Pd(3)–Te(1)–Te(2)	51.66(3)	Te(1)–Pd(1)–Te(3)	94.41(5)
Pd(1)–Te(1)–Te(2)	52.43(4)	P(2)–Pd(2)–Te(2)	96.2(1)
Pd(2)–Te(1)–Te(2)	52.56(4)	P(2)–Pd(2)–Te(1)	170.9(1)
Pd(3)–Te(2)–Pd(1)	86.05(5)	Te(2)–Pd(2)–Te(1)	74.91(4)
Pd(3)–Te(2)–Pd(2)	92.89(5)	P(2)–Pd(2)–Te(3) [a]	100.7(1)
Pd(1)–Te(2)–Pd(2)	80.99(5)	Te(2)–Pd(2)–Te(3) [a]	162.69(5)
Pd(3)–Te(2)–Te(1)	52.55(4)	Te(1)–Pd(2)–Te(3) [a]	88.37(4)
Pd(1)–Te(2)–Te(1)	52.62(3)	P(3)–Pd(3)–Cl(1)	94.4(1)
Pd(2)–Te(2)–Te(1)	52.53(3)	P(3)–Pd(3)–Te(2)	97.3(1)
C(1)–Te(3)–Pd(2) [a]	109.6(4)	Cl(1)–Pd(3)–Te(2)	168.2(1)
C(1)–Te(3)–Pd(1)	97.6(4)	P(3)–Pd(3)–Te(1)	171.4(1)
Pd(2) [a]–Te(3)–Pd(1)	110.83(5)	Cl(1)–Pd(3)–Te(1)	92.5(1)
P(1)–Pd(1)–Te(2)	98.3(1)	Te(2)–Pd(3)–Te(1)	75.79(4)
P(1)–Pd(1)–Te(1)	173.0(1)		

[a] Symmetry transformation: $-x+1/2$, $-y+1/2$, $-z+1$.

tural with the former complex. The complex **3** also shows an analogous molecular framework as $[Pd_6Te_6(PPh_3)_8]$ [6].

The structure is composed of two Pd_3Te_2 fragments that are similar to those found in pentanuclear cations $[M\{Pd_2Te_2(dppe)_2\}_2]^{2+}$ (M = Pd, Pt) [32,33]. The same geometry is also observed in $[Pt_3Te_2(PEt_3)_6]^{2+}$ [34] and $[Pt_3Te_2(dppe)_3]^{2+}$ [35]. It is also worth noting that Fenske et al. [36–38] have shown the existence of a similar Pd_3Se_2 framework in a series of multinuclear palladium complexes.

The two Pd_3Te_2 units in **3** are joined together into a cyclic hexanuclear complex by two bridging $PhTe^-$ ligands. The hexanuclear framework seems to provide an inherently stable structure. Indeed, it has been discussed by Brennan et al. [6] that there is a direct relationship between the Pd_6Te_6 framework and the lattice of binary PdTe.

The Pd–(μ_3-Te) bond lengths in **3** span a range of 2.561(1)–2.603(1) Å (average 2.592 Å). This is expectedly in good agreement with the Pd–(μ_3-Te) distances found in $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ (2.5615(9)–2.6113(8) Å) and $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (2.5909(7)–2.6361(7) Å) [13], $[Pd\{Pd_2Te_2(dppe)_2\}_2]^{2+}$ {2.595(2)–2.619(2) Å [32]; and $[Pd_6Te_6(PEt_3)_8]$ 2.591(1)–2.637(1) Å [6]}. The Pd–Te distances involving $PhTe^-$ ligands seem to be somewhat longer (2.629(2)–2.647(2) Å) in agreement with 2.6286(10)–2.6452(9) Å in $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$, 2.6137(7)–2.6594(7) Å in $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ [13], and 2.630(1)–2.636(1) Å in $[Pd_6Te_6(PEt_3)_8]$ [6].

There is a close Te(1)···Te(2) contact of 3.164(1) Å in **3** (the sum of van der Waals' radii of two tellurium atoms is 3.6 Å [26]). This kind of chalcogen–chalcogen interaction has also been observed in other complexes containing a similar M_3E_2 core (M = Ni, Pd, Pt; E = S, Se, Te) [6,13,33–39].

The Pd–P distances in **1**–**3** [2.284(2), 2.3130(9)–2.3485(9), and 2.302(4)–2.311(4), respectively] and the Pd–Cl distances of 2.3468(9) Å in **2** and 2.422(4) Å in **3** indicate normal single bonds. The small differences can again be explained by the effects of the relative *trans*-influence. The bond lengths within the ligands are also quite normal.

3.3. NMR specroscopy

The reaction of Ph_2Se_2 and $[Pd(PPh_3)_4]$ in dichloromethane produces a mixture exhibiting two major ^{31}P resonances at 28.9 and 27.9 ppm. In addition there are weak resonances at 27.1, 27.0, and a very weak signal at 25.3 ppm. The weak resonances at 30.2 and −3.4 ppm were assigned to Ph_3PO and PPh_3, respectively [12,13].

We have assigned previously two ^{31}P resonances at 29.9 and 29.3 ppm to *cis*- and *trans*-isomers of $[Pd_2(SeTh)_4(PPh_3)_2]$ [12]. The two strongest resonances at 28.9 and 27.9 ppm can therefore be assigned to the two isomers of $[Pd_2(SePh)_4(PPh_3)_2]$. The *trans*-isomer is obtained as the main product upon recrystallization. The weaker resonances at 27.1 and 27.0 ppm can be assigned tentatively to either the two isomers of $[Pd(SePh)_2(PPh_3)_2]$ or those of $[PdCl(SePh)(PPh_3)_2]$. The former can be expected to act as intermediates along the reaction coordinate to the dinuclear complex **1**, and traces of *trans*-$[PdCl(SePh)(PPh_3)_2]$ have been obtained upon recrystallization. The weak resonance at 25.2 ppm is probably due to *trans*-$[PdCl(Ph)(PPh_3)_2]$ that can be expected to be formed in small amounts. The analogous *trans*-$[PdCl(Th)(PPh_3)_2]$ has been obtained as a minor product upon the reaction of Th_2Se_2 and $[Pd(PPh_3)_4]$ in dichloromethane and has been structurally characterized by X-ray crystallography [13]. Its ^{31}P chemical shift in dichloromethane lies at 25.0 ppm.

The reaction of Ph_2Te_2 and $[Pd(PPh_3)_4]$ affords several products exhibiting a rich ^{31}P-NMR spectrum. Furthermore, the spectrum of the redissolved crystals of $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]$ (**3**) is also complicated implying decomposition of the hexanuclear framework in solution, as also observed earlier in the case of $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ and $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ [13]. Up to present it has not been possible to make a meaningful assignment of the spectra.

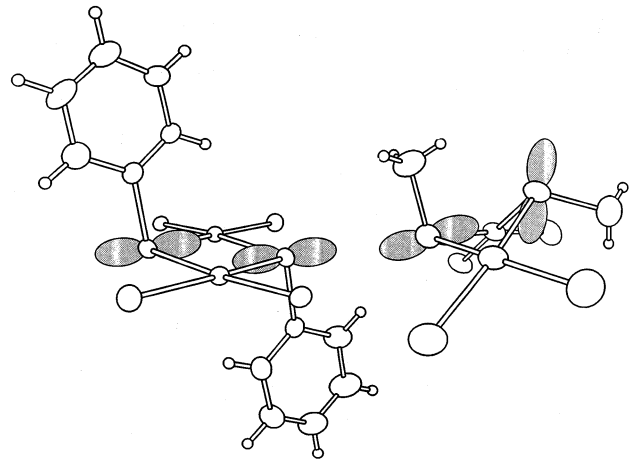


Fig. 4. The pπ lone-pair interactions in the >M(μ-SeR)$_2$M< unit (a) coplanar arrangement (R = Ph) and (b) hinged arrangement (R = Me; molecular conformation taken from Ref. [25]).

4. Discussion

The pathway of the oxidative addition reaction of diaryl dichalcogenides to zerovalent platinum and palladium centers is dependent on the choice of the metal, the chalcogen element, the aryl group, and the solvent. The main products in these reactions are summarized in Table 4.

The most significant single factor affecting the product distribution is the chemical identity of the chalcogen atoms in the starting dichalcogenide. The oxidative addition of R_2Se_2 (R = Ph, Th) to $[M(PPh_3)_4]$ (M = Pd, Pt) mainly leads to the cleavage of the Se–Se bond with the formation of mononuclear and dinuclear complexes the latter of which are probably formed through condensation of the mononuclear complexes [13]. While the reaction with the zerovalent platinum center mainly leads to a mixture of isomers of mononuclear $[Pt(SeR)_2(PPh_3)_2]$ [12,44] and the dinuclear $[Pt_2(SeTh)_4(PPh_3)_2]$ complex is only formed in small amounts, that with palladium affords $[Pd_2(SeR)_4(PPh_3)_2]$ (R = Th, Ph) as the main product. This indicates that some Se–C(aryl) bond cleavage also takes place during the reaction. Some $[PdCl(SePh)(PPh_3)_2]$ (**2**) is also formed upon addition of Ph_2Se_2 to $[Pd(PPh_3)_4]$[2]. Furthermore, $[Pd(SePh)_2(PPh_3)_2]$ might also be present in the reaction mixture.

The presence of monomeric chlorine-containing complexes might also lead to dinuclear complexes containing bridging chloro ligands in addition to bridging arylselenolato ligands. While such complexes have not been observed in the present reaction mixtures, some examples have been prepared, isolated, and structurally characterized by related reaction routes [19,39,40].

Several products are formed during the reaction of diaryl ditelluride and $[M(PPh_3)_4]$ (M = Pt, Pd). There is clear cumulative evidence that the cleavage of the C–Te bond takes place much more readily than that of the C–Se bond (see Table 4 and Refs. [8–14]).

The reaction of R_2Te_2 (R = Th) with platinum in dichloromethane affords $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ and $[PtCl(Th)(PPh_3)_2]$ in equimolar amounts [13]. That with palladium leads to hexanuclear $[Pd_6Cl_2Te_4(TeR)_2(PPh_3)_6]$ {R = Ph, Th [13]}. When $[Pd(PPh_3)_4]$ was treated with dithienyl ditelluride in toluene, $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ containing the same framework was formed. The solvent apparently plays an active role in the C–Te bond cleavage, as has recently been discussed by Khanna et al. [11]. This kind of interaction

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[2] Khandelwal and Gupta [45] have proposed on the basis of elemental analysis and molecular weight determination that **2** is also formed upon the reaction of polymeric $[PdCl(SePh)]_n$ with an excess of PPh_3.

Table 4
The main products in the oxidative addition reactions of R_2E_2 (E = Se, Te; R = Th, Ph) to $[M(PPh_3)_4]$ (M = Pd, Pt) in dichloromethane (side products are shown in italics)

	Se		Te	
	Th[a]	Ph	Th[b]	Ph
Pd	$[Pd_2(SeTh)_4(PPh_3)_2]$[c] *$[PdCl(Th)(PPh_3)_2]$*[c]	$[Pd_2(SePh)_4(PPh_3)_2]$[d] *$[PdCl(SePh)(PPh_3)_2]$*	$[Pd_2(TeTh)_4(PPh_3)_2]$[e] $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_2]$ $[Pd_6Te_4(TeTh)_4(PPh_3)_2]$[f]	$[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_2]$
Pt	$[Pt(SeTh)_2(PPh_3)_2]$ *$[Pt_2(SeTh)_4(PPh_3)_2]$*	$[Pt(SePh)_2(PPh_3)_2]$[g]	$[Pt_3Te_2(Th)(PPh_3)_5]Cl$ $[PtCl(Th)(PPh_3)_2]$	

[a] Ref. [12].
[b] Ref. [13].
[c] When the reaction is carried out in toluene, only $[Pd_2(SeTh)_4(PPh_3)_2]$ is formed.
[d] It has been proposed that $[Pd_2(SePh)_4(PPh_3)_2]$ is also formed in benzene. There is no structural data; see Ref. [16].
[e] The reaction has been carried out in benzene. The identity of the product is based on elemental analysis; see Ref. [43].
[f] The reaction has been carried out in toluene.
[g] The product is obtained upon the oxidative addition of Ph_2Se_2 to $[Pt(H_2C=CH_2)(PPh_3)_2]$; see Ref. [44].

finds support in the preparation and structural characterization of [PdCl(CH_2Cl)(PPh_3)$_2$] in dichloromethane [41]. Species like [MCl(R)(PPh_3)$_2$] have been suggested to be an important factor in the catalytic activity of palladium and platinum complexes [42].

The more complicated polynuclear complexes are probably formed from mono- and dinuclear complexes by successive condensation reactions [13], as initially suggested by Brennan et al. [6], who formulated a pathway for the formation on hexanuclear [Pd_6Te_6(PEt_3)$_8$] with a dinuclear intermediate [Pd_2Te_4(PEt_3)$_4$] [6,7]. Because [Pd_6Te_4(TeR)$_2$(PPh_3)$_6$] contains the same framework as [Pd_6Te_6(PEt_3)$_8$], their formation probably goes through similar stages. The suggested formation of [Pd_2(TeTh)$_4$(PPh_3)$_2$] from Th_2Te_2 and [Pd(PPh_3)$_4$] in benzene [43] lends credibility to this reaction pathway.

The use of [Pt(PPh_3)$_4$] as a reagent with R_2Te_2 again leads to complexes of lower nuclearity than that of [Pd(PPh_3)$_4$]. In an analogous manner, the addition of organic disulfides to the zerovalent platinum center mainly affords mononuclear complexes, while that with Pd(0) results in the formation of dinuclear complexes [46]. Mononuclear palladium complexes could be stablized with strongly electronwithrawing aryl groups.

5. Conclusions

The oxidative addition of tetrakis(triphenylphosphine)palladium and platinum with diaryl dichalcogenides is a complicated process. The product distribution depends on the choice of chalcogen element, metal center, aryl group, and solvent. The most important single factor is the identity of chalcogen atom. While diselenides add to [M(PPh_3)$_4$] mainly with the cleavage of the Se–Se bond forming mononuclear or dinuclear complexes, ditellurides react with the cleavage of both C–Te and Te–Te bonds resulting in the formation of complexes with more complicated structures. Palladium generally has a tendency towards higher nuclearity than platinum. The solvent may also play an active part in the reaction and its choice affects the product distribution.

6. Supplementary material

Crystallographic data for the structural analysis for complexes **1**–**3** (excluding tables of structure factors) have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 150176–150178, respectively. Copies of this information can 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).

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