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The X-ray crystallographic study of the reaction of bis(2-thienyl)ditelluride with tetrakis(triphenylphosphine)platinum or -palladium

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Abstract

The oxidative addition of dithienyl ditelluride to $[Pt(PPh_3)_4]$ in dichloromethane results in the formation of a trinuclear complex $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (Th = 2-thienyl, C_4H_3S) (**1**) as well as a mononuclear complex $[PtCl(Th)(PPh_3)_2]$ that have been identified and structurally characterized by X-ray crystallography and ^{31}P-NMR spectroscopy. The analogous reaction involving $[Pd(PPh_3)_4]$ forms a mixture of several products. In dichloromethane $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ (**2**) can be isolated and its X-ray structure determined. In toluene $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (**3**) is formed. Both **2** and **3** have a similar hexanuclear framework which has previously been reported for $[Pd_6Te_6(PEt_3)_8]$ in the literature. These products indicate that the cleavage of both Te–Te and C–Te bonds as well as the choice of the solvent play an important role in the oxidative addition. The trinuclear and hexanuclear complexes can be considered to be formed from an initial mononuclear addition product. The reaction pathways are compared to those involved in the reaction of Th_2Se_2 and $[M(PPh_3)_4]$ (M = Pt, Pd). © 2000 Elsevier Science S.A. All rights reserved.

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

1. Introduction

The oxidative addition of the organochalcogen compounds to low-valent transition metal centers most often result in the cleavage of the chalcogen–chalcogen bond and the formation of mono- or dinuclear complexes with anionic bridging or terminal RE^- (E = Se, Te) ligands, as reviewed recently by Gysling [1] and Hope and Levason [2]. There are indications, however, that the reaction of aryl ditellurides with zero-valent Group 8 metals may result in the cleavage of the carbon–chalcogen bond [3–6]. The oxidative addition of organochalcogen compounds to low-valent transition metal centers is of interest, as it may be an initial step in homogeneous catalysis [7].

We have recently reported that, while the reaction of $[Pd(PPh_3)_4]$ with Th_2Se_2 (Th = thienyl, C_4H_3S) affords mainly dinuclear $[Pd_2(SeTh)_4(PPh_3)_2]$ with two terminal and two bridging $ThSe^-$ ligands, the main product in the corresponding reaction with $[Pt(PPh_3)_4]$ is mononuclear $[Pt(SeTh)_2(PPh_3)_2]$ with only traces of the dinuclear complex [8]. The solvent also seems to play an active role, as indicated by the formation of small amounts of $[PdCl(Th)(PPh_3)_2]$, when the former reaction was carried out in dichloromethane. This observation also provides evidence that the oxidative addition of Pd(0) may take place through the cleavage of the carbon–chalcogen bond.

We are undertaking a systematic investigation of the factors affecting the pathway of the oxidative addition of aromatic dichalcogenides to zero-valent platinum and palladium centers. This paper is concerned with the reaction of bis(2-thienyl) ditelluride with tetrakis(triphenylphosphine)platinum and -palladium. The reaction with ditelluride is much more complicated than that with diselenide. Some of the reaction products are identified and characterized by X-ray diffraction and ^{31}P-NMR spectroscopy.

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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. CH_2Cl_2 was distilled on CaH_2 and purged with argon before use. Other solvents were purged with argon before use. $[Pd(PPh_3)_4]$ and $[Pt(PPh_3)_4]$ (Aldrich) were used without further purification. Bis(2-thienyl) ditelluride was prepared as described by Engman and Cava [9].

2.2. The reaction of $[Pt(PPh_3)_4]$ with Th_2Te_2

The reaction was carried out by adding Th_2Te_2 (0.076 g, 0.18 mmol) in 5 cm^3 of dichloromethane to 20 cm^3 of a CH_2Cl_2 solution of $[Pt(PPh_3)_4]$ (0.223 g, 0.18 mmol). The reaction mixture was stirred overnight, the solvent was removed by evaporation, and the yellow precipitate was washed with hexane several times. The precipitate was extracted with CH_2Cl_2 and filtered. Upon slow evaporation of the solvent, yellow crystals of $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (**1**) and $[PtCl(Th)(PPh_3)_2]$ were obtained among the amorphous material. The latter complex could be isolated by use of flash chromatography utilizing the Al_2O_3 column (hexane–dichloromethane eluant) and has previously been structurally characterized [10].

2.3. The reaction of $[Pd(PPh_3)_4]$ with Th_2Te_2

The reaction was performed in dichloromethane as described above by using 0.205 g (0.18 mmol) $[Pd(PPh_3)_4]$ and 0.075 g (0.18 mmol) of Th_2Te_2. The product was separated as a dark brown precipitate that turned out to be a mixture of several species. The purification was attempted by solvent extraction and by flash chromatography, but no satisfactory purification was achieved. The reaction was repeated without the precipitation stage, and the mixture was allowed to stand at room temperature for 1 week. During this time dark black–red crystals of $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ (**2**) deposited. When toluene was used as a solvent instead of CH_2Cl_2, black–red crystals of $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (**3**) were obtained. The crystals of **2** and **3** selected for X-ray structure determination contained $\frac{1}{2}CH_2Cl_2$ and $3\frac{1}{2}C_7H_8$, respectively[1].

2.4. NMR spectroscopy

The $^{31}P\{H\}$ spectra were recorded on a Bruker DPX400 spectrometer operating at 161.98 MHz. The spectral width was 58.480 kHz and the respective pulse width was 8.55 μs corresponding to a nuclear tip angle of 45°. The pulse delay was 1.0 s. The ^{31}P accumulation contained ca. 5000–10 000 transients. $CDCl_3$ or benzene-d_6 was used as an internal ^2H lock. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4(aq.).

2.5. X-ray crystallography

Diffraction data for **1**–**3** were collected on a Nonius Kappa CCD diffractometer at 293 K using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) by recording 360 frames via φ-rotation ($\Delta\varphi = 1°$; two times 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 [11] and refined using SHELXL-97 [12]. The thienyl ring in **1** and that of the bridging $ThTe^-$ ligand in **3** were found to be orientationally disordered. In the refinement the disorder was taken into account and the site occupation factors of each disordered pair were refined by constraining their sum 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. The positional parameters of the disordered pairs of atoms were also constrained 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 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 is available as supplementary material.

3. Results and discussion

3.1. General

The oxidative addition of dithienyl ditelluride to $[Pt(PPh_3)_4]$ or $[Pd(PPh_3)_4]$ is complicated and affords several different products. The reaction of Th_2Te_2 and $[Pt(PPh_3)_4]$ in dichloromethane produces ionic $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (**1**) and $[PtCl(Th)(PPh_3)_2]$ the lat-

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[1] Yield in both cases, ca. 20%. Elemental analyses: Anal. Calc. for $C_{116}H_{96}Cl_2P_6Pd_6S_2Te_6\cdot\frac{1}{2}CH_2Cl_2$: C, 42.96; H, 3.00; S, 1.97. Found: C, 41.62; H, 2.48; S, 2.58%. Anal. Calc. for $C_{124}H_{102}P_6Pd_6S_4Te_8\cdot3\frac{1}{2}C_7H_8$: C, 45.87; H, 3.37; S, 3.30. Found: C, 43.27; H, 3.08; S, 3.51%. The observed discrepancy is attributable to the facile evaporation of solvent molecules from the lattice. The parallel X-ray structure determinations from several crystals indicate varying amounts of solvent molecules in the lattice.

Table 1
Details of the structure determination of $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (**1**), $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ (**2**) and $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (**3**)

	1	**2**·$\frac{1}{2}CH_2Cl_2$	**3**·$3\frac{1}{2}C_7H_8$
Empirical formula	$C_{94}H_{78}ClP_5STe_2Pt_3$	$C_{58.25}H_{48}Cl_{1.50}P_3SPd_3Te_3$	$C_{148.5}H_{130}P_6S_4Te_8Pd_6$
Relative molecular mass	2294.91	1628.11	3887.78
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (Å)	14.612(3)	22.538(5)	15.2902(2)
b (Å)	14.657(3)	22.145(4)	18.9235(4)
c (Å)	23.084(5)	23.920(5)	24.9563(4)
α (°)	101.48(3)		76.065(1)
β (°)	101.16(3)	104.42(3)	83.934(1)
γ (°)	102.21(3)		88.876(1)
V (Å^3)	4589.8(2)	11 562(4)	6969.1(2)
Z	2	8	2
F(000)	2176	6224	3734
$D_{calc.}$ (g cm^{-3})	1.643	1.871	1.853
μ(Mo–K$_\alpha$) (mm^{-1})	5.364	2.632	2.578
Crystal size (mm)	0.25 × 0.25 × 0.15	0.40 × 0.20 × 0.05	0.35 × 0.20 × 0.15
θ Range (°)	1.47–25.00	4.08–26.44	2.23–25.00
Number of reflections collected	9033	20 968	70 793
Number of unique reflections	9033	11 506	22 946
Number of observed reflections [a]	6301	3311	17 369
Number of parameters/restraints	975/10	624/0	1437/10
R_{int}	–	0.0664	0.0548
R_1 [b]	0.0705	0.0321	0.0406
wR_2 [b]	0.1719	0.0581	0.0995
R_1 (all data)	0.1114	0.1159	0.0641
wR_2 (all data)	0.2116	0.0636	0.1153
Goodness-of-fit	1.157	0.477	0.866
Max and min heigthts in final difference Fourier synthesis (e Å^{-3})	2.002, −2.113	0.850, −0.647	1.655, −2.288

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

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

ter of which have recently been structurally characterized [10]. In dichloromethane the analogous reaction with $[Pd(PPh_3)_4]$ affords hexanuclear $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ (**2**) among other, as yet unidentified, products. In toluene the main product is $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (**3**). All complexes are air stable.

3.2. $[Pt_3Te_2(Th)(PPh_3)_5]Cl$

The molecular structure and the numbering of the atoms in the cation of $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (**1**) are shown in Fig. 1. The selected bond distances and angles are listed in Table 2.

The cation of **1** has a similar Pt_3Te_2 core to those determined previously for $[Pt_3Te_2(PEt_3)_6]Cl_2$, $[Pt_3Te_2(PEt_3)_6](PF_6)_2$ [13], and $[Pt_3Te_2(dppe)_3](BPh_4)_2$ [14]. All platinum atoms show a slightly distorted square-planar coordination. The sums of the four bond angles around the platinum atoms are 360.40, 363.69, and 359.95° for Pt(1), Pt(2), and Pt(3), respectively (see Table 2). The Pt–Te bond lengths span a range of 2.617(2)–2.643(2) Å (average 2.630 Å), the Pt–P bond lengths span a range of 2.266(7)–2.296(7) Å (average 2.285 Å), and the Pt–C(thienyl) bond exhibits a length of 2.12(3) Å. These values are comparable to the lengths of the corresponding bonds in $[Pt_3Te_2(PEt_3)_6]Cl_2$ (average Pt–Te is 2.633 and Pt–P 2.286 Å) and $[Pt_3Te_2(PEt_3)_6](PF_6)_2$ (average Pt–Te is 2.604 and Pt–P 2.278 Å) [13], as well as in $[Pt_3Te_2(dppe)_3](BPh_4)_2$ (average Pt–Te is 2.634 and Pt–P 2.289 Å [14]. Each

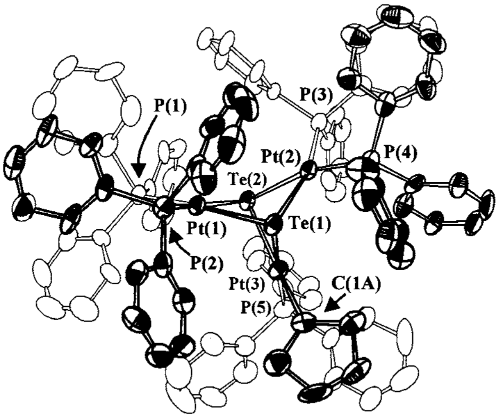

Fig. 1. The molecular structure of $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (**1**) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 50% probability.

Table 2
Selected bond lengths (Å) and angles (°) for $[Pt_3Te_2(Th)\ (PPh_3)_5]Cl$ (**1**)

Bond lengths	
Pt(1)–P(1)	2.276(6)
Pt(1)–P(2)	2.296(7)
Pt(1)–Te(2)	2.622(2)
Pt(1)–Te(1)	2.643(2)
Pt(2)–P(4)	2.289(6)
Pt(2)–P(3)	2.296(7)
Pt(2)–Te(1)	2.617(2)
Pt(2)–Te(2)	2.642(2)
Pt(3)–C(1A) [a]	2.12(3)
Pt(3)–P(5)	2.266(7)
Pt(3)–Te(1)	2.617(2)
Pt(3)–Te(2)	2.637(2)
Te(1)–Te(2)	3.291(2)
Bond angles	
P(1)–Pt(1)–P(2)	99.0(2)
P(1)–Pt(1)–Te(2)	94.19(18)
P(2)–Pt(1)–Te(2)	166.14(17)
P(1)–Pt(1)–Te(1)	170.25(18)
P(2)–Pt(1)–Te(1)	89.86(18)
Te(2)–Pt(1)–Te(1)	77.36(6)
P(4)–Pt(2)–P(3)	100.5(2)
P(4)–Pt(2)–Te(1)	93.53(19)
P(3)–Pt(2)–Te(1)	164.34(16)
P(4)–Pt(2)–Te(2)	165.02(18)
P(3)–Pt(2)–Te(2)	90.19(16)
Te(1)–Pt(2)–Te(2)	77.47(6)
C(1A) [a]–Pt(3)–P(5)	87.5(6)
C(1A) [a]–Pt(3)–Te(1)	89.3(6)
P(5)–Pt(3)–Te(1)	176.8(2)
C(1A) [a]–Pt(3)–Te(2)	166.8(6)
P(5)–Pt(3)–Te(2)	105.6(2)
Te(1)–Pt(3)–Te(2)	77.55(6)
Pt(3)–Te(1)–Pt(2)	80.40(6)
Pt(3)–Te(1)–Pt(1)	83.29(6)
Pt(2)–Te(1)–Pt(1)	91.07(7)
Pt(1)–Te(2)–Pt(3)	83.28(6)
Pt(1)–Te(2)–Pt(2)	90.98(6)
Pt(3)–Te(2)–Pt(2)	79.57(6)

[a] Atom C(1B) constrained in the same position.

polynuclear complex shows an approximate trigonal bipyramidal geometry as exemplified for **1** in Fig. 1. The Pt···Pt distances are very long and do not indicate interaction between the platinum atoms. It is interesting to note, however, that Pt(1)···Pt(3) and Pt(2)···Pt(3) are significantly shorter (3.378 and 3.495 Å) than Pt(1)···Pt(2) (3.754 Å). This asymmetry is a consequence of Pt(3) coordinating to an anionic thienyl ligand that is sterically less demanding than triphenylphosphine. In $[Pt_3Te_2(PEt_3)_6]^{2+}$ [13] and $[Pt_3Te_2(dppe)_3]^{2+}$ [14] the platinum atoms are in similar environments and therefore all three Pt···Pt contacts are closer together, as exemplified by the range 3.388(2)–3.561(1) Å in $[Pt_3Te_2(dppe)_3]^{2+}$ [14]. The packing effects probably also play a role in the non-bonding Pt···Pt distances.

The Te(1)···Te(2) of 3.291(2) Å is shorter than the sum of van der Waals radii of 3.6 Å [15] consistent with $[Pt_3Te_2(PEt_3)_6]^{2+}$ and $[Pt_3Te_2(dppe)_3]^{2+}$ (3.172–3.234 Å [13] and 3.432 Å [14], respectively). Despite the short distance the electron count in the bonding implies the coordination of two μ_3-Te^{2-} ligands with three platinum(II) centers (d^8 ions).

All bond parameters involving the ligands are quite normal. The Cl^- counterion is found disordered in two positions with the occupation factor of 0.5 for both positions. The nearest anion–cation distance is 2.631 Å (Cl(1)···H(223)).

The final difference Fourier map shows the presence of nine weak peaks with a height of 2.00–1.76 e Å^{-3} that are not near any heavy atoms. While these peaks cannot be refined, they indicate a presence of disordered solvent molecule CH_2Cl_2 in the lattice. The site occupation factors are well below 0.5.

The ^{31}P-NMR spectrum of the hand-picked, yellow crystals that are dissolved in chloroform shows three resonances at 15.1, 13.3, and 13.0 ppm together with satellites due to coupling to platinum. Their respective intensity ratio is 1:2:2. The resonance at 15.1 ppm ($^1J_{PtP} = 3839$ Hz; relative intensity 1) is due to P(5) (see Fig. 1) that is coordinated to Pt(3) that also carries the thienyl ligand. It is expectedly at the lowest field. The resonances at 13.3 and 13.0 ppm ($^1J_{PtP} = 3090$ and 3258 Hz, respectively; relative intensity 2 in both cases) are due to two pairs of equivalent phosphorus atoms (P(1), P(2) and P(3), P(4)). It is not, however, possible to assign these resonances further.

3.3. $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ and $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$

The molecular structure and the numbering of the atoms in $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ are shown in Fig. 2 and those of $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ in Fig. 3. The selected bond distances and angles are listed in Table 3.

Both complexes show similar molecular structures even though they are not isostructural. They both contain two Pd_3Te_2 cores that show the same geometry as $[Pt_3Te_2(PEt_3)_6]^{2+}$ [13], $[Pt_3Te_2(dppe)_3]^{2+}$ [14], and $[Pt_3Te_2(Th)(PPh_3)_5]^+$ (**1**). The Pd_3Te_2 core is also found in pentanuclear cations $[M\{Pd_2Te_2(dppe)_2\}_2]^{2+}$ (M = Pd, Pt) [16,17]. The two Pd_3Te_2 fragments in **2** and **3** are joined together into a cyclic hexanuclear complex by two bridging $ThTe^-$ ligands. The main difference in the structures of **2** and **3** is the coordination of Cl^- ligand to Pd(3) in **2**, while in **3** the same position is occupied by a terminal $ThTe^-$ ligand. The overall geometry of the complex is similar to that established for $[Pd_6Te_6(PEt_3)_8]$ [18]. The hexanuclear framework seems to provide an inherently stable structure. Indeed, it has been discussed by Brennan et al. [18] that there is a direct relationship between the Pd_6Te_6 framework and the lattice of binary PdTe.

Each palladium atom in both **2** and **3** also shows a slightly distorted square-planar coordination that is typical for Pd^{II} (the sums of the four bond angles around each metal center range from 359.50 to 360.42°; see Table 3). In **2** the Pd–(μ_3-Te) bond lengths span a range of 2.5616(9)–2.6112(8) Å (average 2.5931 Å). In **3** the corresponding distances are 2.5909(7)–2.6361(7) Å (average 2.6059 Å). This is in good agreement with the Pd–(μ_3-Te) distances found in $[M\{Pd_2Te_2(dppe)_2\}_2]^{2+}$ (M = Pd: 2.595(2)–2.619(2) Å, average 2.607 Å [16]; M = Pt: 2.599(1)–2.636(1) Å, average 2.617 Å [17]) and $[Pd_6Te_6(PEt_3)_8]$ (2.591(1)–2.637(1) Å, average 2.615 Å [18]). The Pd–Te distances involving $ThTe^-$ ligands seem to be somewhat longer (2.6285(10)–2.6452(9) Å in **2** and 2.6137(7)–2.6594(7) Å in **3**), though some overlap in the bond length ranges is evident. This can be compared to the Pd–(μ_2-Te) distances of 2.630(1)–2.636(1) Å in $[Pd_6Te_6(PEt_3)_8]$ [18]. The Pd–P bond lengths in **2** range of 2.309(2)–2.315(2) Å (average 2.317 Å) and in **3** 2.293(2)–2.312(2) Å (average 2.305 Å). They are comparable to Pd–P bonds in analogous complexes (2.261(6)–2.298(6), 2.260(3)–2.295(3), and 2.274(4)–2.323(4) Å for $[Pd\{Pd_2Te_2(dppe)_2\}_2]^{2+}$, $[Pt\{Pd_2Te_2(dppe)_2\}_2]^{2+}$ [16,17] and $[Pd_6Te_6(PEt_3)_8]$ [18], respectively). The Pd(3)–Cl(1) distance of 2.412(2) Å in **2** and all bonds within the ligands are quite normal single bonds.

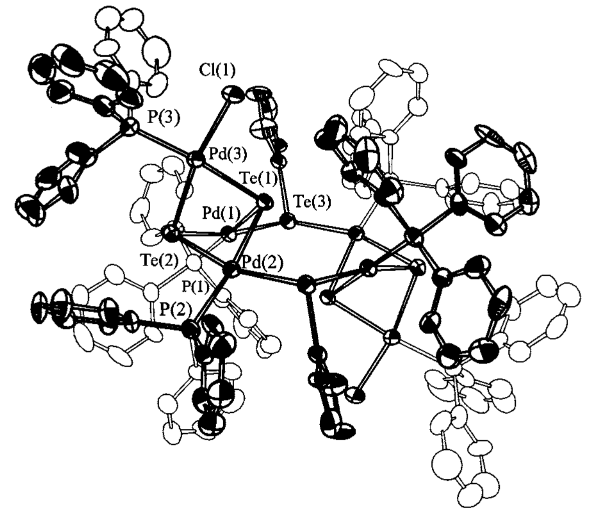

Fig. 2. The molecular structure of $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ (**2**) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 50% probability.

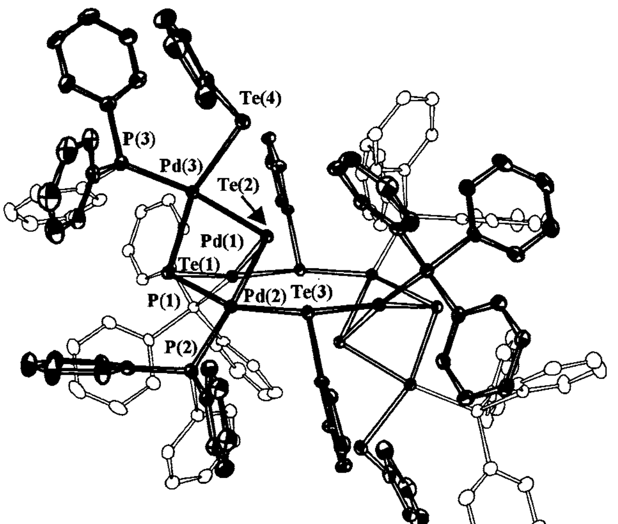

Fig. 3. The molecular structure of $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (**3**) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 50% probability.

Like the Pt···Pt contacts in **1**, the long Pd···Pd distances imply non-bonding character also in **2** and **3** and exhibit similar asymmetry (Pd(1)···Pd(2) are 3.3555 and 3.3339–3.3720 Å for **2** and **3**, respectively, Pd(1)···Pd(3) are 3.5616 and 3.4610–3.6784 Å, and Pd(2)···Pd(3) 3.7338 and 3.6448–3.7474 Å). There are short Te(1)···Te(2) contacts both in **2** and **3** (3.1593(8) and 3.1998(7)–3.2382(6) Å, respectively). Like in **1**, the electron count implies that all palladium atoms are coordinated to two μ_3-Te^{2-} ligands rather than to one Te_2^{2-}.

3.4. Reaction pathways

The oxidative addition reaction of diaryl dichalcogenides to zero-valent platinum and palladium centers has turned out to be complex and its pathway is dependent on the choice of the metal, the chalcogen element, the aryl group, and the solvent. While it is not possible to present a detailed reaction mechanism, the accumulation of data enables the discussion of the formation of the main building blocks.

The oxidative addition of Th_2Se_2 to $[Pt(PPh_3)_4]$ and $[Pd(PPh_3)_4]$ is a relatively clean process and mainly leads to the cleavage of the Se–Se bond, though there is evidence that a simultaneous Se–C(aryl) bond cleavage may also take place to a small extent [8]. Whereas in the case of $[Pt(PPh_3)_4]$, the main product is a mixture of isomers of mononuclear $[Pt(SeTh)_2(PPh_3)_2]$, the reaction of Th_2Se_2 with $[Pd(PPh_3)_4]$ mainly affords dinuclear $[Pd_2(SeTh)_4(PPh_3)_2]$. This is consistent with an earlier report that while the oxidative addition of organic disulfides to zero-valent platinum center affords only mononuclear complexes, that with Pd(0) results in the formation of dinuclear complexes [19]. It was also observed, however, that mononuclear palladium complexes could be formed, when strongly electron-withdrawing aryl groups were used.

The reaction of dithienyl ditelluride and $[M(PPh_3)_4]$ (M = Pt, Pd) is more tangled. Several products seem to be formed during the reaction, and in most cases it has been possible to identify only some reaction products.

Table 3
Selected bond lengths (Å) and angles (°) for $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ (**2**), and $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (**3**)

$[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]\cdot\frac{1}{2}CH_2Cl_2$	
Bond lengths	
Te(1)–Pd(3)	2.5953(10)
Te(1)–Pd(1)	2.6023(9)
Te(1)–Pd(2)	2.6112(8)
Te(1)–Te(2)	3.1594(8)
Te(2)–Pd(3)	2.5616(9)
Te(2)–Pd(1)	2.5926(11)
Te(2)–Pd(2)	2.5958(11)
Te(3)–C(1)	2.131(8)
Te(3)–Pd(2) [b]	2.6285(10)
Te(3)–Pd(1)	2.6452(9)
Pd(1)–P(1)	2.309(2)
Pd(2)–P(2)	2.327(2)
Pd(2)–Te(3) [b]	2.6285(10)
Pd(3)–P(3)	2.315(2)
Pd(3)–Cl(1)	2.412(2)
Bond angles	
Pd(3)–Te(1)–Pd(1)	86.51(3)
Pd(3)–Te(1)–Pd(2)	91.63(3)
Pd(1)–Te(1)–Pd(2)	80.13(3)
Pd(3)–Te(1)–Te(2)	51.74(2)
Pd(1)–Te(1)–Te(2)	52.40(2)
Pd(2)–Te(1)–Te(2)	52.42(2)
Pd(3)–Te(2)–Pd(1)	87.42(3)
Pd(3)–Te(2)–Pd(2)	92.76(3)
Pd(1)–Te(2)–Pd(2)	80.60(3)
Pd(3)–Te(2)–Te(1)	52.70(2)
Pd(1)–Te(2)–Te(1)	52.68 (2)
Pd(2)–Te(2)–Te(1)	52.87(2)
C(1)–Te(3)–Pd(2) [b]	110.5(2)
C(1)–Te(3)–Pd(1)	97.71(18)
Pd(2) [b]–Te(3)–Pd(1)	111.92(3)
P(1)–Pd(1)–Te(2)	98.33(6)
P(1)–Pd(1)–Te(1)	172.95(6)
Te(2)–Pd(1)–Te(1)	74.91(3)
P(1)–Pd(1)–Te(3)	92.85(6)
Te(2)–Pd(1)–Te(3)	167.28(3)
Te(1)–Pd(1)–Te(3)	94.08(3)
P(2)–Pd(2)–Te(2)	95.52(7)
P(2)–Pd(2)–Te(1)	170.04(7)
Te(2)–Pd(2)–Te(1)	74.71(3)
P(2)–Pd(2)–Te(3) [b]	101.67(7)
Te(2)–Pd(2)–Te(3) [b]	162.46(3)
Te(1)–Pd(2)–Te(3) [b]	88.21(3)
P(3)–Pd(3)–Cl(1)	94.40(9)
P(3)–Pd(3)–Te(2)	97.27(7)
Cl(1)–Pd(3)–Te(2)	168.28(7)
P(3)–Pd(3)–Te(1)	170.65(6)
Cl(1)–Pd(3)–Te(1)	92.95(6)
Te(2)–Pd(3)–Te(1)	75.56(2)
$[Pd_6Te_4(TeTh)_4(PPh_3)_6]\cdot3\frac{1}{2}C_7H_8$	
Bond lengths	
Te(1)–Pd(2)	2.6033(7)
Te(1)–Pd(1)	2.6156(7)
Te(1)–Pd(3)	2.6361(7)
Te(1)–Te(2)	3.2382(6)
Te(2)–Pd(3)	2.5909(7)
Te(2)–Pd(1)	2.5957(7)
Te(2)–Pd(2)	2.5971(7)
Te(3)–C(1A) [a]	2.113(8)
Te(3)–Pd(1)	2.6234(7)
Te(3)–Pd(2) [c]	2.6594(7)
Te(4)–C(5)	2.086(9)
Te(4)–Pd(3)	2.6380(8)
Pd(1)–P(1)	2.312(2)
Pd(2)–P(2)	2.293(2)
Pd(2)–Te(3) [c]	2.6594(7)
Pd(3)–P(3)	2.305(2)
Te(1′)–Pd(1′)	2.6009(7)
Te(1′)–Pd(2′)	2.6030(7)
Te(1′)–Pd(3′)	2.6078(7)
Te(1′)–Te(2′)	3.1998(7)
Te(2′)–Pd(1′)	2.5967(7)
Te(2′)–Pd(3′)	2.6028(7)
Te(2′)–Pd(2′)	2.6211(7)
Te(3′)–C(1′)	2.103(7)
Te(3′)–Pd(2′) [d]	2.6173(7)
Te(3′)–Pd(1′)	2.6444(7)
Te(4′)–C(5′)	2.110(9)
Te(4′)–Pd(3′)	2.6205(8)
Pd(1′)–P(1′)	2.309(2)
Pd(2′)–P(2′)	2.312(2)
Pd(2′)–Te(3′) [d]	2.6173(7)
Pd(3′)–P(3′)	2.300(2)
Bond angles	
Pd(2)–Te(1)–Pd(1)	80.50(2)
Pd(2)–Te(1)–Pd(3)	82.68(2)
Pd(1)–Te(1)–Pd(3)	91.05(2)
Pd(2)–Te(1)–Te(2)	51.402(16)
Pd(1)–Te(1)–Te(2)	51.306(17)
Pd(3)–Te(1)–Te(2)	51.095(17)
Pd(3)–Te(2)–Pd(1)	92.53(2)
Pd(3)–Te(2)–Pd(2)	83.69(2)
Pd(1)–Te(2)–Pd(2)	80.99(2)
Pd(3)–Te(2)–Te(1)	52.349(17)
Pd(1)–Te(2)–Te(1)	51.860(17)
Pd(2)–Te(2)–Te(1)	51.572(16)
C(1A) [a]–Te(3)–Pd(1)	108.98(19)
C(1A) [a]–Te(3)–Pd(2) [c]	99.51(19)
Pd(1)–Te(3)–Pd(2) [c]	110.02(2)
C(5)–Te(4)–Pd(3)	109.5(3)
P(1)–Pd(1)–Te(2)	96.49(5)
P(1)–Pd(1)–Te(1)	173.30(5)
Te(2)–Pd(1)–Te(1)	76.83(2)
P(1)–Pd(1)–Te(3)	100.03(5)
Te(2)–Pd(1)–Te(3)	163.48(3)
Te(1)–Pd(1)–Te(3)	86.64(2)
P(2)–Pd(2)–Te(2)	91.65(5)
P(2)–Pd(2)–Te(1)	168.33(5)
Te(2)–Pd(2)–Te(1)	77.03(2)
P(2)–Pd(2)–Te(3) [c]	93.92(5)
Te(2)–Pd(2)–Te(3) [c]	170.27(3)
Te(1)–Pd(2)–Te(3) [c]	96.90(2)
P(3)–Pd(3)–Te(2)	96.44(6)
P(3)–Pd(3)–Te(1)	170.50(6)
Te(2)–Pd(3)–Te(1)	76.56(2)
P(3)–Pd(3)–Te(4)	102.81(6)
Te(2)–Pd(3)–Te(4)	160.75(3)
Te(1)–Pd(3)–Te(4)	84.31(2)
Pd(1′)–Te(1′)–Pd(2′)	79.68(2)
Pd(1′)–Te(1′)–Pd(3′)	88.82(2)
Pd(2′)–Te(1′)–Pd(3′)	89.81(2)
Pd(1′)–Te(1′)–Te(2′)	51.944(17)
Pd(2′)–Te(1′)–Te(2′)	52.487(17)
Pd(3′)–Te(1′)–Te(2′)	52.043(17)
Pd(1′)–Te(2′)–Pd(3′)	89.02(2)
Pd(1′)–Te(2′)–Pd(2′)	79.43(2)
Pd(3′)–Te(2′)–Pd(2′)	89.52(2)
Pd(1′)–Te(2′)–Te(1′)	52.062(17)
Pd(3′)–Te(2′)–Te(1′)	52.186(17)
Pd(2′)–Te(2′)–Te(1′)	51.973(17)
C(1′)–Te(3′)–Pd(2′) [d]	112.2(2)
C(1′)–Te(3′)–Pd(1′)	96.4(2)
Pd(2′) [d]–Te(3′)–Pd(1′)	114.11(2)
C(5′)–Te(4′)–Pd(3′)	105.8(2)
P(1′)–Pd(1′)–Te(2′)	171.21(6)
P(1′)–Pd(1′)–Te(1′)	95.45(5)
Te(2′)–Pd(1′)–Te(1′)	75.99(2)
P(1′)–Pd(1′)–Te(3′)	94.37(5)
Te(2′)–Pd(1′)–Te(3′)	94.09(2)
Te(1′)–Pd(1′)–Te(3′)	169.84(3)
P(2′)–Pd(2′)–Te(1′)	96.92(5)
P(2′)–Pd(2′)–Te(3′) [d]	102.47(5)
Te(1′)–Pd(2′)–Te(3′) [d]	159.94(3)
P(2′)–Pd(2′)–Te(2′)	171.21(6)
Te(1′)–Pd(2′)–Te(2′)	75.54(2)
Te(3′) [d]–Pd(2′)–Te(2′)	85.49(2)
P(3′)–Pd(3′)–Te(2′)	171.03(6)
P(3′)–Pd(3′)–Te(1′)	95.26(6)
Te(2′)–Pd(3′)–Te(1′)	75.77(2)
P(3′)–Pd(3′)–Te(4′)	102.51(6)
Te(2′)–Pd(3′)–Te(4′)	86.43(2)
Te(1′)–Pd(3′)–Te(4′)	162.09(3)

[a] Atom C(1B) constrained in the same position.
[b] Symmetry transformation: $-x+1/2$, $-y+1/2$, $-z+1$.
[c] Symmetry transformations: $-x$, $-y+1$, $-z+1$.
[d] Symmetry transformations: $-x+1$, $-y+1$, $-z$.

It is evident, however, that in addition to the cleavage of the Te–Te bond, the simultaneous cleavage of the C–Te bond takes place much more readily than that of the C–Se cleavage.

The reaction of Th_2Te_2 and $[Pt(PPh_3)_4]$ in dichloromethane affords two main products. In addition to $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (**1**) a chalcogen-free $[PtCl(Th)(PPh_3)_2]$ (**4**) was also obtained. The isolation, identification, and structural characterization of the latter complex have recently been reported [10]. The formation of both **1** and **4** imply C–Te bond cleavage. It also indicates that the solvent plays an active role in the reaction, since dichloromethane is the only source of chlorine in the reaction system. It has recently been reported that the reaction of Ph_2Te and $[M(PEt_3)_4]$ (M = Ni, Pd, Pt) results in the Te–C bond cleavage and

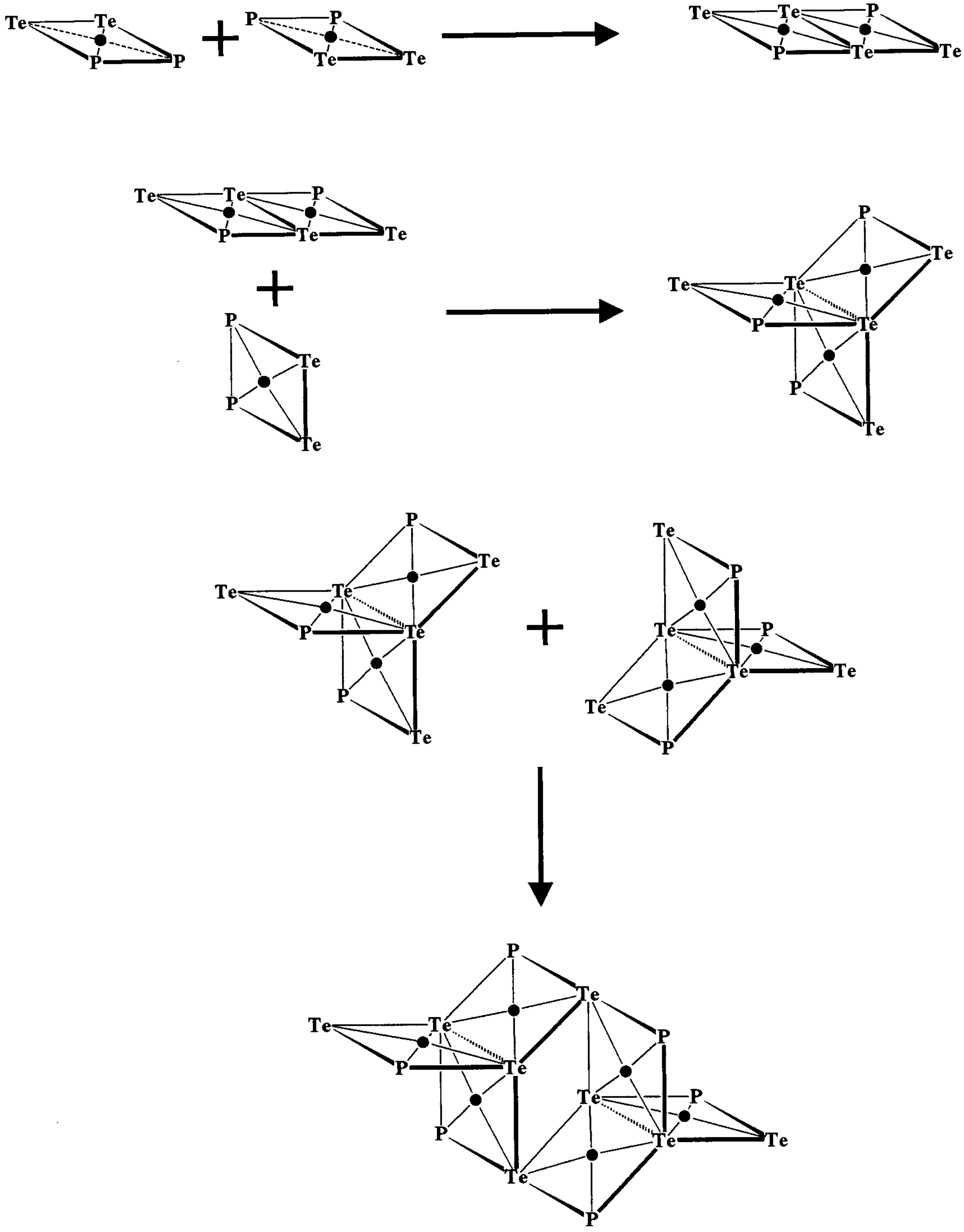

Fig. 4. The relationship between the dinuclear, trinuclear, and hexanuclear complexes as exemplified by the formation of **3**. The scheme has been modified from that presented by Brennan et al. [18]. Only donor atoms in the ligands have been indicated.

the formation of $[M(TePh)(Ph)(PEt_3)_2]$ [3]. The active role of the dichloromethane in the C–Te bond cleavage has recently been discussed by Khanna et al. [6]. This kind of interaction finds support in the preparation and structural characterization of $[PdCl(CH_2Cl)(PPh_3)_2]$ [20]. Xie et al. [21] suggested that the formation of species like **4** is an important factor in the catalytic activity of palladium and platinum complexes.

The reaction of Th_2Te_2 with $[Pd(PPh_3)_4]$ has been carried out both in dichloromethane and in toluene and the composition of the reaction mixture was monitored as a function of time by use of ^{31}P-NMR spectroscopy. In both cases the spectra indicated several products. Furthermore, the compositions of both reaction mixtures slowly changed as a function of time. In dichloromethane the only product that could be isolated and crystallized was $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ (**2**). In the toluene solution $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (**3**) was formed. These products are again consistent with the simultaneous cleavage of both Te–Te and Te–C bonds. The participation of dichloromethane in the reaction is also evident in the case of **2**.

The formation of hexanuclear $[Pd_6Te_6(PEt_3)_8]$ that contains the same framework as **2** and **3** has been shown to proceed through a dinuclear intermediate $[Pd_2Te_4(PEt_3)_4]$ [18,22] It is therefore conceivable that there is a dinuclear intermediate also in the pathway to **2** and **3**. Indeed, Chia and McWhinnie [23] have suggested the formation of a dinuclear $[Pd_2(TeTh)_4(PPh_3)_2]$ in the reaction of Th_2Te_2 and $[Pd(PPh_3)_4]$ in benzene.

The pathway leading to the hexanuclear complex **3** is shown in Fig. 4. It is adapted from the scheme presented by Brennan et al. [18]. It involves a step of oxidative addition upon which a mononuclear complex is formed. Such a reaction is known to take place between Th_2Se_2 and $[Pt(PPh_3)_4]$ with the formation of both *cis* and *trans* isomers of $[Pt(SeTh)_2(PPh_3)_2]$ [8]. The mutual condensation of two *cis* or *trans* complexes leads to a dinuclear complex $[Pt_2(SeTh)_4(PPh_3)_2]$.[2] In Fig. 4 this condensation step is exemplified by two *cis* complexes. Further condensation steps create first the trinuclear complex with a geometry that has been observed for the cation of **1**, and finally the hexanuclear structure **3**. A similar scheme can be utilized to explain the formation of **1** and **2**. It is probable that in dichloromethane $[MCl(Th)(PPh_3)_2]$ ($M = Pd$, Pt) takes an active part in the condensation processes.

The appearance of μ_3-Te^{2-} ligands in **1**–**3** can also be explained as follows: It is well known that PPh_3 can abstract sulfur from polysulfides with the formation of Ph_3PS and ultimate degradation of the polysulfide chain length [24]. It can be seen by ^{31}P-NMR spectroscopy that there is free PPh_3 in each reaction mixture. It is conceivable that PPh_3 can abstract tellurium from dithienyl ditelluride with the formation of Ph_3PTe that is not stable and decomposes releasing tellurium.

4. Conclusions

This paper reports the reactions of tetrakis(triphenylphosphine)palladium and -platinum with dithienyl ditelluride as part of a systematic investigation of the factors affecting the pathways of oxidative addition of aromatic dichalcogenides to zero-valent palladium and platinum centers. The reactions involving dithienyl ditelluride are more complicated than those involving dithienyl diselenide and result in the formation of several products as a consequence of the cleavage of both Te–Te and C–Te bonds. Some main products could be identified and structurally characterized by X-ray crystallography.

The oxidative addition of Th_2Te_2 to $[Pt(PPh_3)_4]$ in dichloromethane affords a trinuclear complex $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (**1**) together with mononuclear $[PtCl(Th)(PPh_3)_2]$. In the reaction of Th_2Te_2 with $[Pd(PPh_3)_2]$ in dichloromethane, hexanuclear $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6]$ (**2**) could be isolated and identified. In toluene, $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (**3**) was obtained.

The Pt_3Te_2 core in **1** has an approximately trigonal bipyramidal arrangement of atoms. The complex can also be viewed as square-planar coordination planes of three platinum atoms sharing a common edge. The hexanuclear frameworks in **2** and **3** are formed upon coupling two M_3Te_2 units together through two bridging $ThTe^-$ ligands. Indeed, the structures of **2** and **3** differ only by **3** having two terminal $ThTe^-$ ligands in place of two Cl^- ligands in **2**.

The combined information of the oxidative addition of Th_2Se_2 [8] and Th_2Te_2 to zero-valent platinum and palladium centers enables some inferences on the reaction pathway to be made. While 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, dithienyl ditelluride reacts with the cleavage of both C–Te and Te–Te bonds resulting in the formation of complexes with more complicated structures.

The choice of solvent seems to be an important factor affecting the reaction pathway. Dichloromethane plays an active role during the reaction affording $[MCl(Th)(PPh_3)_2]$ that can also participate in the reaction.

The possible co-existence of $[M(TeTh)_2(PPh_3)_2]$, $[MCl(Th)(PPh_3)_2]$, $ThTe^-$, and Ph_3Pte (Te) in the reac-

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[2] In the case of $[Pd(PPh_3)_4]$ and Th_2Se_2 the reaction leads immediately to the dinuclear $[Pd_2(SeTh)_4(PPh_3)_2]$. No mononuclear complex can be detected in this reaction [8].

tion mixture provides the necessary building blocks for the formation of $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (**1**) and $[Pd_6X_2Te_4(TeTh)_2(PPh_3)_2]$ ($X = Cl^-$ (**2**), $ThTe^-$ (**3**)). The formation of **1**–**3** can be explained by successive condensation reaction steps from the initial mononuclear oxidative addition product. The present results confirm that palladium has a tendency towards higher nuclearity than platinum.

5. Supplementary material

Crystallographic information for complexes **1**–**3** (excluding tables of structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC nos. 133172–133174, 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).

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References

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

[2] E.G. Hope, W. Levason, Coord. Chem. Rev. 122 (1993) 109.

[3] L.-B. Han, N. Choi, M. Tanaka, J. Am. Chem. Soc. 119 (1997) 1795.

[4] L.-B. Han, S. Shimada, M. Tanaka, J. Am. Chem. Soc. 119 (1997) 8133.

[5] L.-B. Han, M. Tanaka, Chem. Commun. (Cambridge) (1998) 47.

[6] A. Khanna, B.L. Khandelwal, A.K. Saxena, T.P. Singh, Polyhedron 14 (1995) 2705.

[7] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, Wiley, New York, 1992.

[8] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgrén, J. Organomet. Chem. 587 (1999) 200.

[9] L. Engman, M.P. Cava, Organometallics 1 (1982) 470.

[10] R. Oilunkaniemi, M. Niiranen, R.S. Laitinen, M. Ahlgrén, J. Pursiainen, Acta Chem. Scand. 52 (1998) 1068.

[11] G.M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997.

[12] G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

[13] A.L. Ma, J.B. Thoden, L.F. Dahl, J. Chem. Soc. Chem. Commun. (1992) 1516.

[14] K. Matsumoto, M. Ikuzawa, M. Kamikubo, S. Ooi, Inorg. Chim. Acta 217 (1994) 129.

[15] J. Emsley, The Elements, Clarendon Press, Oxford, 1998.

[16] K. Matsumoto, C. Nishitani, M. Tadokoro, S. Okeya, J. Chem. Soc. Dalton Trans. (1996) 3335.

[17] C. Nishitani, T. Shizuka, K. Matsumoto, S. Okeya, H. Kimoto, Inorg. Chem. Commun. 1 (1998) 325.

[18] J.G. Brennan, T. Siegrist, S.M. Stuczynski, M.L. Steigerwald, J. Am. Chem. Soc. 112 (1990) 9233.

[19] R. Zanella, R. Ros, M. Graziani, Inorg. Chem. 12 (1973) 2736.

[20] O.J. Scherer, H. Jungmann, J. Organomet. Chem. 208 (1981) 153.

[21] Y. Xie, B.-M. Wu, F. Xue, S.C. Ng, T.C.W. Mak, T.S.A. Hor, Organometallics 17 (1998) 3988.

[22] M.L. Steigerwald, S.M. Stuczynski, Y.-U. Kwon, D.A. Vennos, J.G. Brennan, Inorg. Chim. Acta 312 (1993) 219.

[23] L.-Y. Chia, W.R. McWhinnie, J. Organomet. Chem. 148 (1978) 165.

[24] D.M. Giolando, M. Papavassiliou, J. Pickardt, T.B. Rauchfuss, R. Steudel, Inorg. Chem. 27 (1988) 2596.