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Cluster Intermediates in an Organometallic Synthesis of PdTe

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Abstract: We show that the binary solid-state compound palladium telluride, PdTe, results from the reaction of tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$, and triethylphosphine telluride, Et_3PTe, in refluxing toluene. When the same reagents are combined in the same solvent at room temperature two molecular compounds can be isolated. We have determined the structure of each of these crystallographically. The smaller molecule, $(Et_3P)_4Pd_2Te_2$, **1**, contains a simple Pd_2Te_2 four-membered ring, and we show that this four-membered ring can be appreciated as a fragment of the PdTe solid lattice. The larger molecule, $(Et_3P)_8Pd_6Te_6$, **2**, has a more complicated structure that can be described as an eight-membered ring that is twice bridged by $(Et_3P)_2PdTe$ units. We rationalize the structure of **2** by comparing it to the structure of PdTe.

The synthesis of inorganic solid-state compounds using molecular starting materials offers a valuable complement to the synthesis from the solid elements.[1] Since the solid-state interdiffusion of the elements is obviated in the molecular process, a significant kinetic restriction is removed. This gives opportunities to prepare previously unknown, metastable materials as well as to prepare previously known materials but under substantially milder conditions. In the attempt to understand the pathways by which molecules form solids, we have been studying molecular syntheses of metal chalcogenides and have previously reported the use of phosphine tellurides in the preparation of the solid-state tellurides of Hg, Cd,[2] Mn,[3] Fe,[4] and Ni.[5] The utility of phosphine tellurides is based on their ability to reversibly deposit elemental tellurium[6] (which is rationalized by their description[7] as coordination complexes of zerovalent Te). Having characterized the reactions of R_3PTe with zerovalent Ni we wished to study the (presumably) milder reaction of R_3PTe with zerovalent Pd (eq 1). In this report we describe a molecular synthesis of PdTe, the interception of two intermediates, $Pd_2Te_2(PEt_3)_4$, **1**, and $Pd_6Te_6(PEt_3)_8$, **2**, and discuss the structure of the solid-state compound in terms of the molecular intermediates.

$$Pd(PPh_3)_4 + TePEt_3 \rightarrow PdTe \qquad (1)$$

Experimental Section

General Methods. Unless otherwise noted all manipulations were carried out under inert atmosphere by using standard drybox or schlenk techniques. Toluene and heptane were anhydrous grade and were used as received from Aldrich. Triethylphosphine and elemental Te were also used as received from Aldrich. Tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) was supplied by Strem Chemicals. Triethylphosphine telluride was prepared as in ref 6.

Synthesis of PdTe from $Pd(PPh_3)_4$ and $TePEt_3$. A solution of $Pd(PPh_3)_4$ (0.46 g, 0.40 mmol) and $TePEt_3$ (0.101 g, 0.41 mmol) in toluene was heated to reflux for 40 min. The resulting precipitate was collected, washed, and dried in vacuo to give 93.3 mg (100%) of PdTe as a dark grey powder. Powder X-ray diffraction showed this and only this phase. Anal. Found (Analytische): Pd (44.60), Te (53.50), C (0.88), H (0.22), P (0.86). Calcd for PdTe: Pd (45.47), Te (54.53).

Isolation of $Pd_2Te_2(PEt_3)_4$, 1, and $Pd_6Te_6(PEt_3)_8$, 2. $Pd(PPh_3)_4$ (1.2 g, 1.0 mmol) was suspended in 50 mL of 4:1 (v:v) heptane/toluene and treated with PEt_3 (1 mL, 0.8 g, 7 mmol) and $TePEt_3$ (0.25 g, 1.0 mmol). After 5 h at room temperature the mixture was filtered and then allowed to stand undisturbed at room temperature for 72 h. During this time dark red crystals of **2** (40 mg, 10%) deposited. (Anal. Found (Schwartzkopf): C (24.4), H (5.06), P (10.2), Pd (25.3), Te (33.6). Calcd for $C_{48}H_{120}P_8Pd_6Te_6$: C (24.5), H (5.15), P (10.5), Pd (27.2), Te (32.6).) This compound is not sufficiently soluble to allow for NMR spectroscopy.

The supernatant liquor from this crystallization was subsequently cooled to −20 °C, and dark green crystals (8 mg, 2%) of **1** deposited. ^1H NMR (C_6D_6, 30 °C) 1.85 (m, 2 H), 0.94 (m, 3 H); ^{31}P NMR (C_6D_6, 30 °C) one singlet 8.4 ppm upfield from free PEt_3.

Table I. $Pd_2Te_2(PEt_3)_4$: Crystallographic Data

compound	$Pd_2Te_2(PEt_3)_4$
empirical formula	$PdTeP_2C_{12}$
formula weight	440.08
crystal system	monoclinic
space group	$P21/n$
a, Å	10.337 (3)
b, Å	13.419 (3)
c, Å	13.955 (5)
β, deg	109.76 (3)
V, Å^3	1821.7 (9)
Z	4
D_{calc}, g/cm^3	1.605
μ(Mo Kα), mm^{-1}	5.25
λ, Å	0.70930
crystal dimensions, mm	0.20 × 0.20 × 0.20
$2\theta_{max}$	40
scan type	ω
data collected	$-0 < h < 9, 0 < k < 12, 0 < l < 13$
no. of reflcns	2157
no. of unique reflctns	1695
no. of reflcns with $I_{net} > 2.5\sigma(I_{net})$	1365
no. of parameters	86
R_f	0.039
R_w	0.040
GOF	3.701
secondary extinction coeff	0.25 (2)

After an additional week at room temperature the supernatant from this latter crystallization deposited an additional 19 mg (5%) of **2**.

Conversion of 2 to PdTe. $Pd_6Te_6(PEt_3)_8$ (12 mg, 5 × 10^{-3} mmol) was heated at 250 °C for 14 h in an evacuated and sealed Pyrex tube. The material did not melt but did change color to grey as the PEt_3 evolved. The grey solid (ca. 6 mg, 85%) was shown by powder X-ray diffraction to be PdTe.

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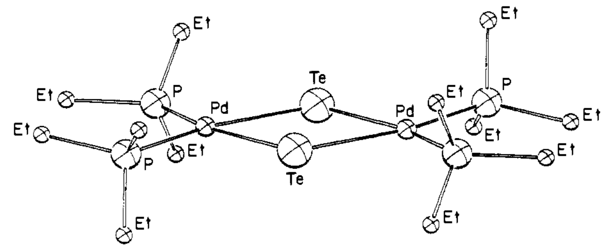


Figure 1. Molecular structure of $[(Et_3P)_2PdTe]_2$. The ethyl groups are represented by just the α-carbon atoms for clarity. Selected distances: Pd–Te, 2.6122 (16) Å; Pd–P(av), 2.325 (4) Å; Te–Te, 3.0657 (21). Selected angles: Te–Pd–Te, 71.86 (4)°; Pd–Te–Pd, 108.14 (5)°; P–Pd–P, 107.81 (15)°.

Table II. $Pd_6Te_6(PEt_3)_8$: Crystallographic Data

compound	$Pd_6Te_6(PEt_3)_8$
empirical formula	$Pd_3Te_3P_4C_{24}$
formula weight	1114.15
crystal system	monoclinic
space group	$P21/n$
a, Å	12.8676 (6)
b, Å	22.2643 (8)
c, Å	14.1466 (6)
β, deg	101.946 (7)
V, Å^3	3965.1 (3)
Z	4
D_{calc}, g/cm^3	1.866
μ(Mo Kα), mm^{-1}	3.67
λ, Å	0.70930
crystal dimensions, mm	0.20 × 0.20 × 0.20
$2\theta_{max}$	50
transmission factors	0.447298–0.618165
scan type	$\theta/2\theta$
data collected	$-14 < h < 14, 0 < k < 26, 0 < l < 16$
no. of reflcns	7690
no. of unique reflcns	6941
no. of reflcns with $I_{net} > 2.5\sigma(I_{net})$	4446
no. of parameters	188
R_f	0.045
R_w	0.036
GOF	2.963
secondary extinction coeff	0.14 (1)

Results and Discussion

Equimolar amounts of $Pd(PPh_3)_4$ and Et_3PTe react in refluxing toluene to give a black powder which was shown by powder X-ray diffraction to be polycrystalline PdTe (eq 1). (This is a fairly mild synthesis of PdTe. Synthesis from the elements requires several days heating at 500 °C or above.) As we found[5] in the case of a similar solution-phase preparation of NiTe, this reaction can be interrupted at the molecular fragment stage by the use of proper reaction conditions. The reaction of $Pd(PPh_3)_4$ and Et_3PTe in toluene at room temperature does not give the solid-state compound, instead we were able to isolate and structurally characterize two Pd/Te molecular compounds, $Pd_2Te_2(PEt_3)_4$, **1**, and $Pd_6Te_6(PEt_3)_8$, **2**. The $(PdTe)_2$ compound is difficult to isolate; the reaction conditions we have used give primarily the $(PdTe)_6$ product. We have not been able to study the reaction chemistry of **1**, but since **2** can be isolated in reasonably large quantities we have been able to show that it can be converted readily to bulk PdTe.

The structure of the Pd_2Te_2 cluster is described in Figure 1 and Table I. This molecule is quite simple, a Pd_2Te_2 rhombus with two phosphine ligands coordinated to each Pd. The bond lengths and angles are consistent with cis square-planar Pd(II) and the absence of Te–Te or Pd–Pd bonding. The Pd–Te bond length (2.61 Å) is close to the sum of covalent radii (2.64 Å), and the Te–Te distance (3.07 Å) is much longer than reported Te–Te bonds (2.7–2.8 Å). The structure of the Pd_6Te_6 cluster is described in Figure 2, Table I, and Table III. This rather open structure has several notable features, perhaps the most curious of which is that even though the molecule is three dimensional each of the six Pd atoms has a coordination environment which is close to square planar. Eight of the twelve Pd and Te atoms (Te_1, Pd_1 through Te_4, Pd_4) form an essentially planar parallelogram. Each of the four Pd atoms in this ring has a single Et_3P ligand external to the ring, and the structure is completed by two $TePd(PEt_3)_2$ units, one above and one below the plane of the eight-membered ring. The Pd–Te distances are all between 2.59 and 2.64 Å, again close to the sum of the covalent radii.

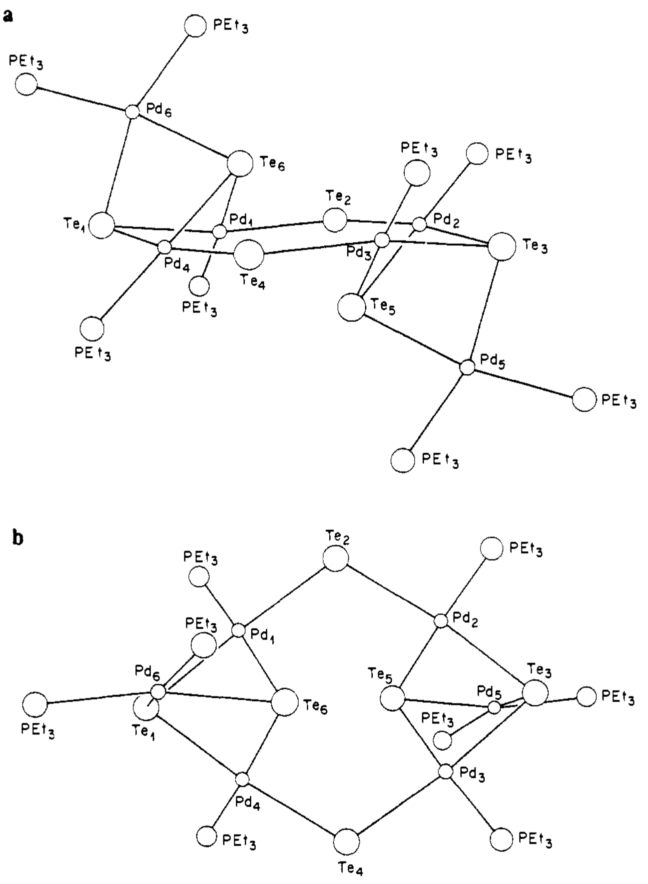


Figure 2. (a) Molecular structure of $(Et_3P)_8Pd_6Te_6$. The ethyl groups are omitted in the interest of clarity. (b) The same structure viewed from above the (approximate) plane of the eight-membered ring.

Table III. Selected Distances and Angles Found in $Pd_6Te_6(PEt_3)_8$[a]

Pd(1)–Te(6)	2.6049 (14)	Pd(6)–P(6)	2.319 (4)
Pd(1)–Te(1)	2.6237 (14)	Pd(6)–P(6a)	2.323 (4)
Pd(1)–Te(2)	2.6357 (14)	Te(6)–Te(5)	3.8283 (17)
Pd(1)–P(1)	2.274 (4)	Te(6)–Te(1)	3.2856 (12)
Pd(4)–Te(6)	2.5913 (13)	Te(6)–Te(2)	3.7779 (13)
Pd(4)–Te(1)	2.6121 (14)	Te(6)–Te(4)	3.7602 (13)
Pd(4)–Te(4)	2.6297 (14)	Te(6)–P(6)	3.446 (4)
Pd(4)–P(4)	2.281 (4)	Te(2)–Pd(2)	2.6297 (14)
Pd(6)–Te(6)	2.6372 (13)	Te(2)–Te(5)	3.7602 (13)
Pd(6)–Te(1)	2.6222 (14)		
Te(6)–Pd(1)–Te(1)	77.86 (4)	Te(6)–Pd(6)–P(6)	87.86 (10)
Te(6)–Pd(1)–Te(2)	92.25 (4)	Te(6)–Pd(6)–P(6a)	164.67 (14)
Te(6)–Pd(1)–P(1)	177.52 (12)	Te(1)–Pd(6)–P(6)	158.23 (11)
Te(1)–Pd(1)–Te(2)	169.13 (6)	Te(1)–Pd(6)–P(6a)	91.29 (14)
Te(1)–Pd(1)–P(1)	99.66 (12)	P(6)–Pd(6)–P(6a)	105.77 (17)
Te(2)–Pd(1)–P(1)	90.22 (12)	Pd(1)–Te(6)–Pd(4)	82.58 (4)
Te(6)–Pd(4)–Te(1)	78.31 (4)	Pd(1)–Te(6)–Pd(6)	81.90 (4)
Te(6)–Pd(4)–Te(4)	92.14 (4)	Pd(4)–Te(6)–Pd(6)	89.73 (4)
Te(6)–Pd(4)–P(4)	176.83 (11)	Pd(1)–Te(1)–Pd(4)	81.82 (4)
Te(1)–Pd(4)–Te(4)	170.35 (5)	Pd(1)–Te(1)–Pd(6)	81.83 (4)
Te(1)–Pd(4)–P(4)	99.10 (10)	Pd(4)–Te(1)–Pd(6)	89.61 (4)
Te(4)–Pd(4)–P(4)	90.49 (10)	Pd(1)–Te(2)–Pd(2)	108.77 (5)
Te(6)–Pd(6)–Te(1)	77.32 (4)		

[a] Numbering scheme shown in Figure 2. The molecule has a center of symmetry such that the symmetry-related pairs are (Te_1, Te_3), (Te_2, Te_4), and (Te_5, Te_6), and similarly for Pd. A complete table of distances and angles is provided in the supplementary material.

The fact that the coordination geometry around Pd is square-planar in both **1** and **2** suggests an alternative description

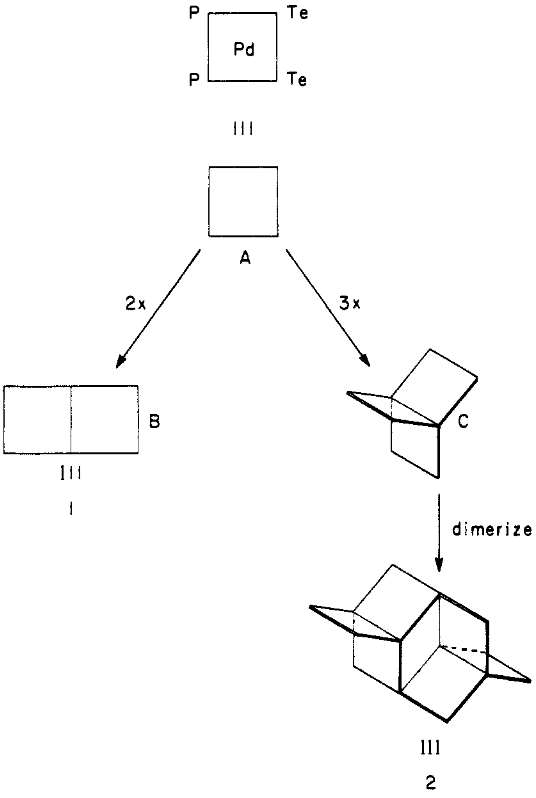


Figure 3. The construction of compounds **1** and **2** from fundamental PdL_4 squares.

of the two structures and emphasizes the strong geometrical relationship between the two. The coordination of Pd by four ligands gives (ideally) a square, A, as shown in Figure 3. The dimerization of such squares can occur by sharing either an edge or a corner. In **1** the two are combined in the former mode to give a planar molecule (represented by B in Figure 3) in which the (nonbonding) Pd–Pd distance has been maximized. The structure of **2** can be visualized by starting with a two-square structure and adding a third square such that the three share a common edge (C in figure 3). Structure **2** (Figure 3) results from the dimerization of C through corner sharing. This structural analysis highlights the importance of square-planar coordination in Pd(II) which is so well-known in molecular chemistry.

It is valuable to relate the structures of **1** and **2** to the structure of crystalline PdTe. In doing so we hope to elucidate at least some aspects of the pathways by which the atomic and molecular reagents assemble into the solid-state lattice. Furthermore, we anticipate that some insight into the bonding, properties, and reactivity of the solid will come from the description of the solid in terms of molecular fragments. We also hope that the structure of the solid will give clues about the structures of the molecules we have isolated.

Stoichiometric PdTe forms in the NiAs structure type.[9] This structure has hexagonal close-packed anions with cations placed in the octahedral holes formed by the anion lattice. In Figure 4a we show the conventional ball-and-stick representation of the PdTe lattice. The relationship between **1** and the PdTe lattice is apparent from this figure since the Pd_2Te_2 unit that is the nucleus of **1** occurs throughout. To clarify this we have redrawn the lattice in Figure 4b, eliminating most of the internuclear "sticks". Figure 4b shows that the PdTe crystal can be thought of as Pd_2Te_2 rhombuses linked together into pleated, stacked sheets. Holm and co-workers[10] have shown recently that a large number of Fe–S clusters can be described as connected Fe–S rhombuses.

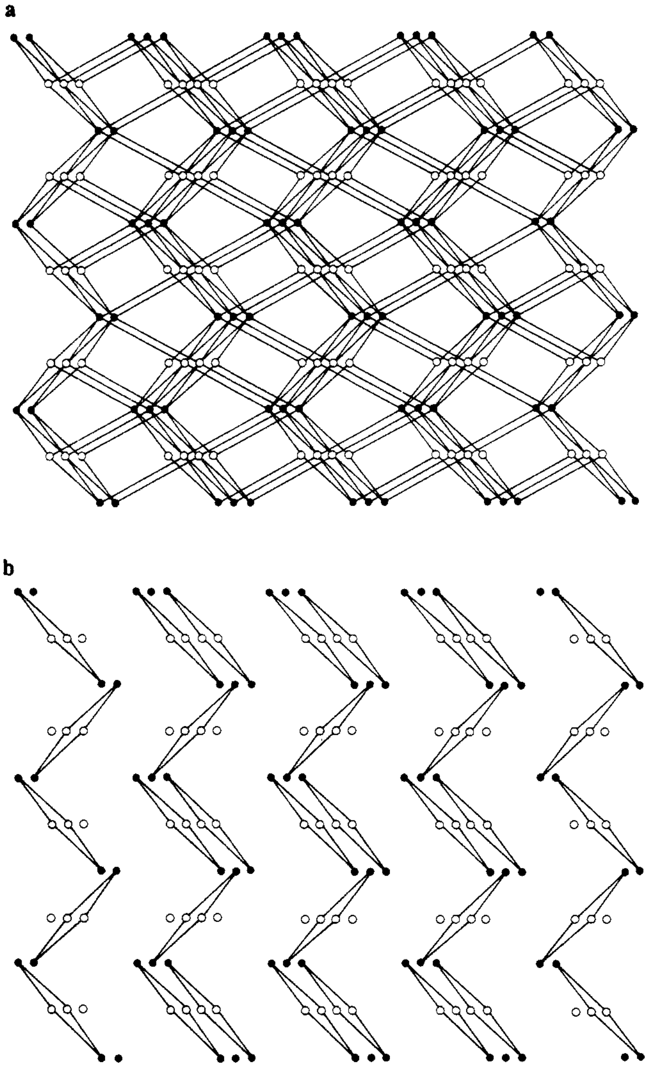
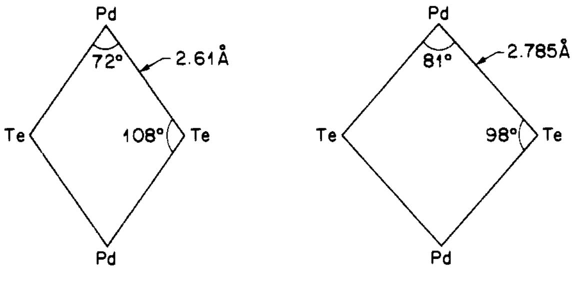


Figure 4. Ball-and-stick representations of the bulk PdTe lattice. The open circles represent Pd atoms and the filled circles Te atoms. Panel (a) includes all of the (equivalent) Pd–Te bonds. Panel (b) is simplified by deleting all but two bonds to each atom.



$Pd_2Te_2(PEt_3)_4$

PdTe BULK

Figure 5. Comparison of the Pd_2Te_2 rhombuses from **1** and bulk PdTe.

The Pd–Te rhombus in **1** and that in PdTe are compared in Figure 5. The angles differ substantially, but the sense of the rhomboidal distortions are the same (acute at Pd, obtuse at Te). The difference can be explained since the PEt_3 is locally bulkier than the corresponding Te donor ligands in PdTe. This is expected to lead to the smaller internal angle at Pd in **1**. In a similar way, since the Te in **1** is two-coordinate while the Te in PdTe is six-coordinate, the angle at Te should be larger in **1** than in PdTe. The Pd–Te distance is much shorter in **1** than in PdTe. This is understandable since each atom in PdTe is six-coordinate. The higher coordination in the solid results in longer bonds.

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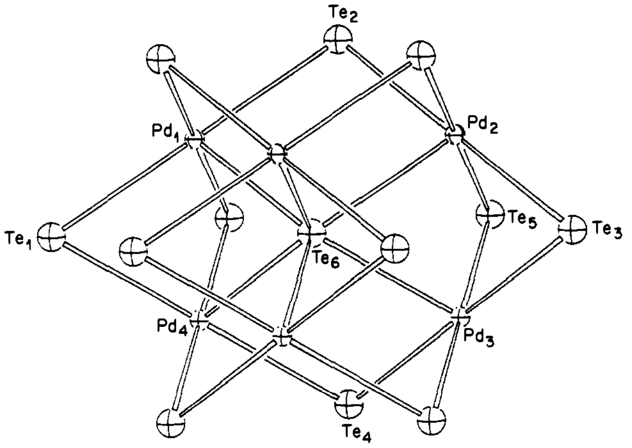

Figure 6. Coordination environments around Te in the bulk PdTe lattice. Pd is represented by small spheres and Te by large spheres.

At first glance the structure of **2** is peculiar, and we hoped that its formation could be rationalized by some correspondence with the PdTe lattice. In Figure 6 we show the local environment around Te in the PdTe lattice, including the central Te, its nearest neighbors (Pd), and closest second nearest neighbors (Te). Establishing a direct structural relationship between **2** and stoichiometric PdTe requires the removal of two Pd atoms from **2** and a distortion of the resulting Pd_4Te_6 framework. Removal of the two out-of-plane Pd atoms (Pd_5 and Pd_6, Figure 2) and subsequent folding of the eight-membered ring along the Te_1–Te_3 diagonal gives a structure which can be recognized as a fragment of the PdTe lattice. The now distorted eight-membered ring (Te_1, Pd_2, through Te_4, Pd_4) can be identified with the similarly numbered eight-membered ring in Figure 6. The two remaining Te atoms in **2** can be identified with Te_5 and Te_6 in Figure 6.

If, instead, the two out-of-plane Pd atoms are retained **2** can be seen directly as a slightly distorted small fragment of the Ni_2In-type lattice. The Ni_2In lattice is referred to as "filled up NiAs"[11] inasmuch as the large voids in NiAs are filled by the "extra" Ni in Ni_2In. We believe this relationship helps to understand the structure of complex **2** as follows. The Pd- and Te-containing reagents begin to assemble the NiAs-type lattice, at the same time maintaining the square-planar coordination geometry favored by Pd(II). Early in the growth process the more densely packed Ni_2In-type lattice, the very close structural relative of the NiAs-type lattice, is preferred, and the observed Pd_6Te_6 unit, a small fragment of the latter structure, is formed. Ultimately the "surface" of this fragment is terminated with phosphine ligands allowing the isolation of **2**.

The variation of the structure of **2** from that of the PdTe lattice can be rationalized in an alternate way. As described above the PdTe lattice grows to the Pd_4Te_6 core. At this point growth at the acidic Pd sites can be terminted by capping with phosphine, but a number of Lewis basic Te sites remain open. The two out-of-plane $Pd(PEt_3)_2$ units add across four of these open Te centers. In this way the PEt_3 ligand is a basic cap for the acidic Pd sites, and the acidic $Pd(PEt_3)_2$ moiety is an acidic cap for the basic Te sites. The $Pd(PEt_3)_2$ unit which bridges Te_1 and Te_6 pulls Te_6 out of the center of the eight-membered ring. The folded eight-membered ring distorts to planarity because the constraint imposed by the remainder of the PdTe lattice is absent and the ring can relax to the sterically less crowded planar geometry. (It is noteworthy that the fold in the ring corresponds to a pleat in the PdTe sheets described in Figure 5).

We are lead to the following conclusions: (1) In the case of PdTe, molecular reaction intermediates mimic the structure of the solid-state crystalline product at a very small size, i.e., very early in the growth process. This is similar to the II–VI compounds (CdS, CdSe, HgTe, etc.)[12] but quite different than, for example, silicon.[13] (2) Changes to the growing PdTe lattice such as the addition of two "extra" Pd atoms in **2** can be rationalized in either of two ways; one based in solid state terms and the other in more molecular terms. In the former compound **2** is viewed as a fragment not of PdTe but of $Pd_{1+x}Te$. In the latter the extra Pd atoms are viewed as acidic caps just as the phosphines are considered basic caps, and both are invoked as simply terminating the PdTe fragment. (3) The PdTe crystal can be interpreted as a very organized polymer of the Pd_2Te_2 rhombus, compound **1** being an isolated, PEt_3-capped, chemically and structurally characterized representative of the monomer.

Supplementary Material Available: Tables listing positional and thermal parameters, significant distances, and angles (7 pages); tables of observed and calculated structure factors (59 pages). Ordering information is given on any current masthead page.

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