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# Initial Stages in the Molecule-Based Growth of the Solid-State Compound CoTe

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*Received April 26, 1991*

The reaction of $Co_2(CO)_8$ with $TePEt_3$ gives $[(Et_3P)_2(CO)_2CoTe]_2$ (**1**), $(Et_3P)_4(CO)_6Co_4Te_2$ (**2**), or $(Et_3P)_6Co_6Te_8$ (**4**), depending on reaction conditions and/or reagent ratios. Heating **4** as a solid in vacuo results in the release of $Et_3P$ and the condensation of the $Co_6Te_8$ units to give the solid-state compound $\beta$-CoTe. We show that **1** reacts with $Co_2(CO)_8$ to give **2** and that **2** reacts with $TePEt_3$ to give **4**. We have determined the structures of **1** and **2** crystallographically: for **1**, monoclinic, space group *C2/c*, $a = 26.288$ (5) Å, $b = 13.533$ (3) Å, $c = 13.291$ (3) Å, $\beta = 100.34$ (3)°, $Z = 8$; for **2**, orthorhombic, space group $P2_12_12_1$, $a = 13.496$ (1) Å, $b = 13.672$ (1) Å, $c = 23.476$ (1) Å, $Z = 4$. With these data, in addition to our previously reported data for **4**, we show that the structure of $\beta$-CoTe evolves as **1** → **2** → **4** and that these reactions may be viewed as the first stages of the growth of the solid-state compound from molecular precursors.

## Introduction

The relationships between isolated molecules and extended solids are intriguing. One reason for this is that molecules and solids are extremes of physical localization and delocalization, respectively. Accepting this, questions arise concerning the paths along which the extremes are connected. One class of questions deals with how the physical properties (bond lengths and angles, electrical, optical, and magnetic behavior, etc.) of particular molecules and the associated solids correlate. The hope is that the understanding of one extreme will amplify the understanding of the other once the correspondence of the two is appreciated. Another class of questions deals with the chemical conversion of molecules into solids. The more that is known about the formation of infinite solids from molecules, the more effectively the molecular precursor method can be used to make new materials.

In this paper we describe an example of the formation of an extended solid from isolated molecular reagents. We use triethylphosphine telluride ($Et_3PTe$) and dicobalt octacarbonyl ($Co_2(CO)_8$) to prepare the solid-state compound $\beta$-CoTe.[1] Studying this molecules-to-solids process, we have isolated three molecular compounds: $(Et_3P)_4(CO)_4Co_2Te_2$ (**1**), $(Et_3P)_4(CO)_6Co_4Te_2$ (**2**), and $(Et_3P)_6Co_6Te_8$ (**4**).

We show that the dicobalt ditelluride **1** reacts with added $Co_2(CO)_8$ to give the tetracobalt ditelluride **2**, that **2** reacts with added $Et_3PTe$ to give the Chevrel-type $Co_6Te_8$ cluster compound **4**, and that **4** reacts thermally to give $\beta$-CoTe. In this way we outline one aspect of the molecule-to-solid transition, the stepwise growth from the molecular starting materials through the molecular intermediates to the ultimate solid product. We show that as the growth proceeds the structure of the solid evolves. The sequence is summarized in Scheme I.

## Results

**(A) Formation and Characterization of $(Et_3P)_2(CO)_2CoTeTeCo(CO)_2(PEt_3)_2$.** The reaction of $Co_2(CO)_8$ with 2 equiv of $Et_3PTe$ in the presence of 2 equiv of $Et_3P$ gives $[(Et_3P)_2(CO)_2CoTe]_2$ (**1**) (eq 1). The reaction is conducted in

$$Co_2(CO)_8 + 2TePEt_3 + 2PEt_3 \rightarrow [(Et_3P)_2(CO)_2CoTe]_2 \quad (1)$$

toluene, with the mixture heated to 100 °C for a short time, and the compound is isolated as a solid. Compound **1** is very soluble in toluene, benzene, and tetrahydrofuran and less so in saturated hydrocarbons. The material can be crystallized from toluene/heptane, with such solutions depositing large crystals of **1** on cooling. As a solid, **1** is green, forming cube-shaped crystals. Crystals from this solvent system were used to determine the structure of **1** crystallographically. Crystal data are shown in Table I, selected bond distances and angles are given in Table II, and a drawing of the dicobalt ditelluride is shown in Figure 1.

**Scheme I**

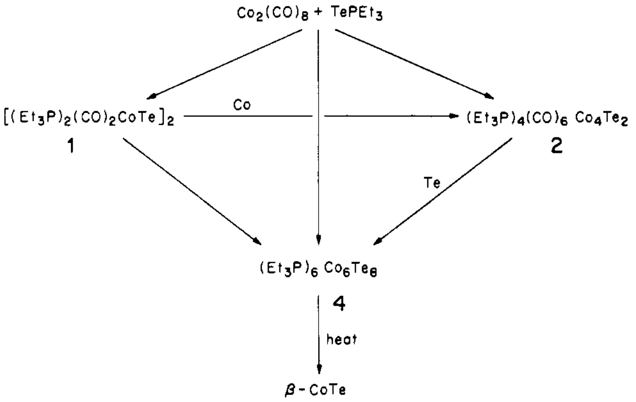

**Table I.** Crystallographic Data for $[(Et_3P)_2(CO)_2CoTe]_2\cdot{}^1/_2C_7H_8$

| | | | |
|---|---|---|---|
| empirical formula | $C_{24}H_{60}Co_2O_4P_4Te_2\cdot{}^1/_2C_7H_8$ | $V$ | 4652 (2) Å$^3$ |
| | | $Z$ | 8 |
| fw | 1003.8 | $T$ | 23 °C |
| space group[a] | *C2/c* | $\rho_{calc}$ | 1.453 Mg/m$^3$ |
| $a$ | 26.288 (5) Å | $\mu$(Mo K$\alpha$) | 2.11 mm$^{-1}$ |
| $b$ | 13.533 (3) Å | $\lambda$ | 0.709 30 Å |
| $c$ | 13.291 (3) Å | $R_F$[b] | 0.059 |
| $\beta$ | 100.34 (3)° | $R_w$[c] | 0.054 |

[a] *C2/c* was discriminated from *Cc* by the analysis of merged intensities. [b] $R_F = \{\sum(F_o - F_c)\}/\{\sum F_o\}$. [c] $R_w = \{\sum w(F_o - F_c)^2\}/\{\sum(wF_o^2)\}$.

**Table II.** Selected Distances and Angles Found for $[(Et_3P)_2(CO)_2CoTe)_2$[a]

| | | | |
|---|---|---|---|
| | Distances (Å) | | |
| Co–Te | 2.614 (2) | Te–Te | 2.765 (2) |
| Co–$P_1$ | 2.212 (4) | Co–$P_2$ | 2.214 (4) |
| Co–$C_1$ | 1.69 (2) | Co–$C_2$ | 1.71 (2) |
| $C_1$–$O_1$ | 1.19 (2) | $C_2$–$O_2$ | 1.19 (3) |
| | Angles (deg) | | |
| Co–Te–Te | 101.70 (5) | Te–Co–$P_1$ | 86.5 (1) |
| Te–Co–$P_2$ | 86.9 (1) | Te–Co–$C_1$ | 130.2 (4) |
| Te–Co–$C_2$ | 114.3 (5) | $C_1$–Co–$C_2$ | 115.5 (7) |
| $P_1$–Co–$P_2$ | 169.9 (2) | $P_1$–Co–$C_1$ | 88.7 (4) |
| $P_1$–Co–$C_2$ | 94.1 (5) | $P_2$–Co–$C_1$ | 89.9 (4) |
| $P_2$–Co–$C_2$ | 95.5 (5) | | |

[a] Atom labeling as in Figure 1. The halves of the molecule are related by symmetry.

The structure of **1** is similar to that of $[(Et_3P)_2(CO)_3MnTe]_2$, which we reported.[2] The coordination geometry around each cobalt is distorted trigonal pyramidal with the phosphines in the apical positions. The Co–Te bond distance is the same as the Co–Te distance in bulk CoTe[1]—slightly longer than the sum of the covalent radii.[3] The Te–Te bond length in **1** is the same as

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[1] Haraldsen, H.; Gronvold, F.; Hurlen, T. *Z. Anorg. Allg. Chem.* **1956**, *283*, 143.

[2] Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 4228.

[3] Pauling L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

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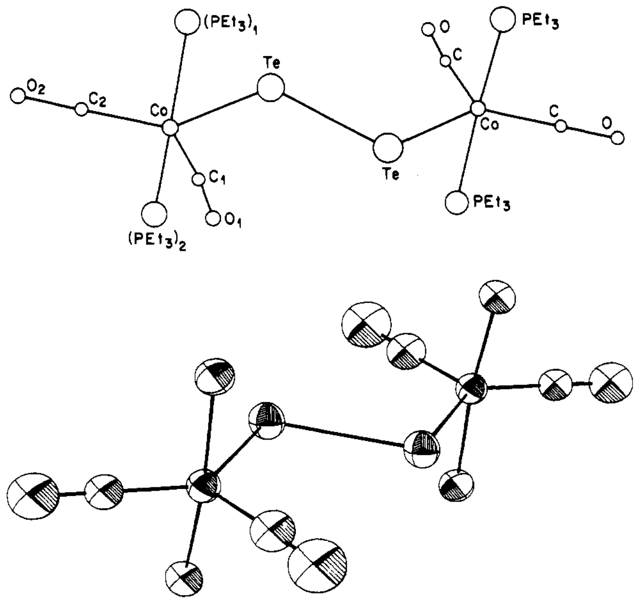

**Figure 1.** (a) Top: Drawing of the molecular structure of $[(Et_3P)_2(CO)_2CoTe]_2$ (**1**). The ethyl groups are omitted for clarity. (b) Bottom: Drawing of **1**, showing thermal vibration ellipsoids.

**Table III.** Crystallographic Data for $(Et_3P)_4(CO)_6Co_4Te_2$

| | | | |
|---|---|---|---|
| empirical formula | $C_{30}H_{60}Co_4O_6P_4Te_2$ | $Z$ | 4 |
| fw | 1071.14 | $T$ | 23 °C |
| space group | $P2_12_12_1$ | $\rho_{calc}$ | 1.642 Mg/m$^3$ |
| $a$ | 13.496 (1) Å | $\mu$(Mo K$\alpha$) | 3.01 mm$^{-1}$ |
| $b$ | 13.672 (1) Å | $\lambda$ | 0.709 30 Å |
| $c$ | 23.476 (1) Å | $R_F$[a] | 0.055 |
| $V$ | 4331.7 (6) Å$^3$ | $R_w$[b] | 0.047 |

[a] $R_F = \{\sum(F_o - F_c)\}/\{\sum F_o\}$. [b] $R_w = \{\sum w(F_o - F_c)^2\}/\{\sum(wF_o^2)\}$.

that in the manganese analogue, each being longer than those in organic ditellurides.[4]

The $^1H$ NMR spectrum of **1** shows only coordinated $Et_3P$. The proton-decoupled $^{31}P$ NMR spectrum of **1** shows a single resonance. We could discern no P–Te coupling satellites. The infrared spectrum of **1** contains two bands in the terminal CO stretching region. The UV–visible absorption spectrum shows two features: a peak centered at 376 nm and a pronounced shoulder at approximately 430 nm. The optical absorptions are quite intense; even very dilute solutions of **1** are optically very dense.

**(B) Formation and Characterization of $(Et_3P)_4(CO)_6Co_4Te_2$.** Compound **1** reacts with $Co_2(CO)_8$ and $Et_3P$ in toluene to give the cluster $(Et_3P)_4(CO)_6Co_4Te_2$ (**2**) (eq 2). The added phosphine

$$[(Et_3P)_2(CO)_2CoTe]_2 + Co_2(CO)_8 + PEt_3 \rightarrow (Et_3P)_4(CO)_6Co_4Te_2 \quad (2)$$

appears to accelerate the process as well as suppress the formation of insoluble byproducts. When equimolar amounts of $Co_2(CO)_8$ and **1** and several equivalents of phosphine are combined in toluene and the mixture is heated, the initially deep yellow-brown color of the mixture quickly changes to a very deep black-red. The cluster **2** can be isolated from this mixture in high yield.

The identical product can be prepared directly from $Co_2(CO)_8$, $Et_3PTe$, and $Et_3P$. When the three are combined in a 1:1:5 molar ratio in toluene and the mixture is heated to reflux, the reaction quickly takes on the same black-red color. The product is isolated by evaporation of the solvent followed by crystallization from toluene/heptane.

The structure of **2** was also determined crystallographically. Crystal data are given in Table III, geometrical data in Table IV, and a drawing of the structure in Figure 2. The molecule is a rectangle of Co atoms (aspect ratio = 1.16), capped above and below the plane with Te atoms. Each Co atom bonds to the two Te atoms, one phosphine, one terminal CO ligand, and one bridging CO ligand. Each bridging CO spans one of the short sides of the $Co_4$ rectangle, and the phosphines are alternately above and below the $Co_4$ plane around the $Co_4$ rectangle.

**Table IV.** Selected Distances and Angles Found for $(Et_3P)_4(CO)_6Co_4Te_2$[a]

| | | | |
|---|---|---|---|
| | Distances (Å) | | |
| $Te_a-Te_b$ | 3.252 (1) | $Te_a-Co_a$ | 2.545 (2) |
| $Te_a-Co_b$ | 2.573 (2) | $Te_a-Co_c$ | 2.572 (2) |
| $Te_a-Co_d$ | 2.549 (2) | $Te_b-Co_a$ | 2.563 (2) |
| $Te_b-Co_b$ | 2.550 (2) | $Te_b-Co_c$ | 2.554 (2) |
| $Te_b-Co_d$ | 2.557 (2) | $Co_a-Co_b$ | 2.583 (3) |
| $Co_a-Co_c$ | 2.988 (3) | $Co_b-Co_d$ | 2.987 (3) |
| $Co_c-Co_d$ | 2.582 (3) | | |
| $(Co-P)_{av}$ | 2.225 (5) | $(Co-C)_{br}$[b] | 1.93 (2) |
| $(Co-C)_t$[b] | 1.73 (2) | | |
| | Angles (deg) | | |
| $Co_a-Te_a-Co_b$ | 60.62 (6) | $Co_a-Te_a-Co_c$ | 71.46 (7) |
| $Co_a-Te_a-Co_d$ | 101.26 (7) | $Co_b-Te_a-Co_c$ | 100.66 (7) |
| $Co_b-Te_a-Co_d$ | 71.36 (7) | $Co_c-Te_a-Co_d$ | 60.57 (6) |
| $Co_a-Te_b-Co_b$ | 60.68 (7) | $Co_a-Te_b-Co_c$ | 71.47 (7) |
| $Co_a-Te_b-Co_d$ | 100.55 (7) | $Co_b-Te_b-Co_c$ | 101.78 (7) |
| $Co_b-Te_b-Co_d$ | 71.59 (7) | $Co_c-Te_b-Co_d$ | 60.70 (6) |
| $Te_a-Co_a-Te_b$ | 79.07 (6) | $Te_a-Co_b-Te_b$ | 78.81 (6) |
| $Te_a-Co_c-Te_b$ | 78.75 (6) | $Te_a-Co_d-Te_b$ | 79.12 (6) |

[a] Atom labeling as in Figure 2. [b] t = terminal; br = bridge.

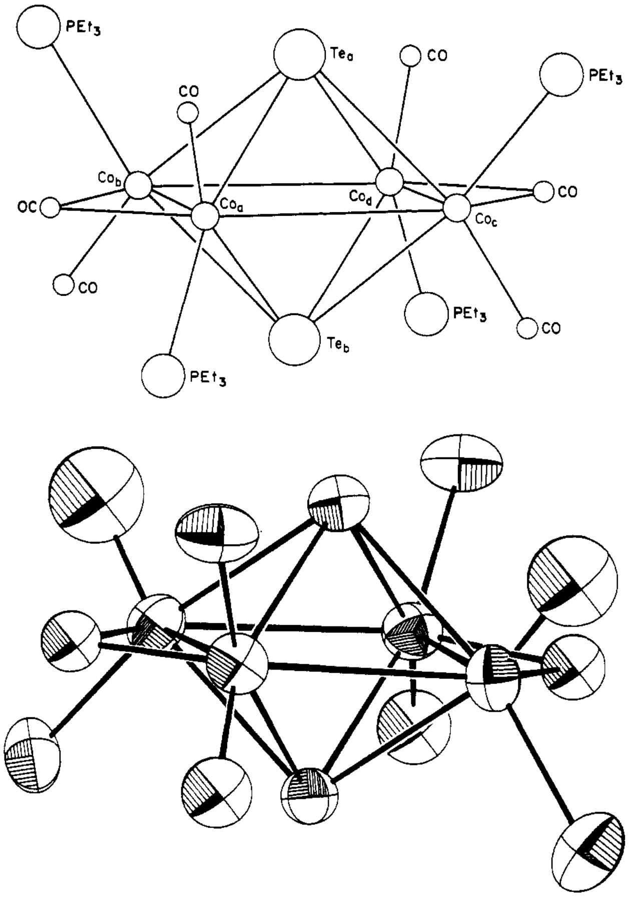

**Figure 2.** (a) Top: Drawing of the molecular structure of $(Et_3P)_4(CO)_6Co_4Te_2$ (**2**). The ethyl groups are omitted for clarity. (b) Bottom: Drawing of **2**, showing thermal vibration ellipsoids.

Compound **2** is a member of the $L_{10}Co_4E_2$ (E = chalcogen) family first reported by Marko and co-workers.[5] The structure of **2** is very similar to that of $(CO)_{10}Co_4Te_2$ reported by Dahl and

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(4) Ludlow, S.; McCarthy, A. E. *J. Organomet. Chem.* **1981**, *219*, 169.

(5) (a) Marko, L.; Bor, G.; Almasy, G. *Chem. Ber.* **1961**, *94*, 847. (b) Marko, L.; Bor, G.; Klumpp, E.; Marko, B.; Almasy, G. *Chem. Ber.* **1963**, *96*, 955. (c) See also: Hieber, W.; Kruck, T. *Chem. Ber.* **1962**, *95*, 2027.

co-workers;[6] structure **2** results from the replacement of one of the terminal CO ligands at each of the Co centers with $Et_3P$. The phosphine substitution leads to a slight elongation of the Co–Te bonds (2.55–2.57 Å versus 2.54 Å) and a more substantial elongation of the longer Co–Co distances (2.99 Å versus 2.88 Å). Each Co–Te bond in **2** is slightly longer than the Co–Te bond in **1**.

The $^1H$ NMR spectrum of **2** shows unexceptional, coordinated $Et_3P$. The proton-decoupled $^{31}P$ NMR spectrum shows a single broad resonance. The infrared absorption spectrum shows two carbonyl stretching bands, a terminal CO stretch (1912 $cm^{-1}$), and a bridging CO stretch (1770 $cm^{-1}$). The UV–visible absorption spectrum is rather complicated, having at least five distinct features at room temperature.

The singular UV–visible absorption spectrum is a simple diagnostic tool. We used it to show that **1** reacts with $Et_3P$ to give **2** (and, presumably, $Et_3PTe$ as the other product). When **1** is treated with an excess of $Et_3P$ in toluene, the bands due to **1** recede while those of **2** grow.

**(C) Formation and Characterization of $(Et_3P)_6Co_6Te_8$.** When **2** is allowed to react with $Et_3PTe$ and $Et_3P$ in refluxing toluene, the color of the reaction mixture changes from very dark black-red to a brighter, yet still optically very dense, cherry red. The product of this reaction, **3**, can be isolated by crystallization from toluene/heptane. (In an earlier paper[7] we reported that the same compound can be prepared from $Co_2(CO)_8$, $Et_3PTe$, and $Et_3P$ directly. The three reagents are combined in toluene in a (roughly) 3:8:13 molar ratio and heated to reflux for 2 h. Subsequent crystallization gives **3**.)

The $^1H$ NMR spectrum of **3** shows only coordinated $Et_3P$. The $^{31}P$ NMR spectrum shows a single very broad resonance. The UV–visible spectrum shows three very intense bands, consistent with the deep color of solutions of **3**. The infrared spectrum of **3** verifies the absence of both **1** and **2**; however, there remains an absorption of variable intensity (at 1930 $cm^{-1}$) that is assignable to a terminal CO ligand. This CO can be replaced with $Et_3P$ by treating **3** with a large excess of the phosphine in refluxing toluene. This gives compound **4** as a crystalline solid. Compound **4** is qualitatively the same as **3** except in the IR spectrum, this showing no CO absorption bands. (In addition, the peaks in the UV–visible absorption spectrum are sharper than those in **3**.) The analysis of **4** shows it to be $(Et_3P)_6Co_6Te_8$; on the basis of these data and observations, we believe **3** to be $L_6Co_6Te_8$, in which the two-electron ligands are a mixture of CO and $PEt_3$. The processes are summarized in eq 3.

$$\begin{tikzcd}
{}^{3}/_{2}[(Et_3P)_4(CO)_6Co_4Te_2] + 5TePEt_3 \arrow[d] & \\
3 \arrow[r] & (Et_3P)_6Co_6Te_8 \\
3Co_2(CO)_8 + 8TePEt_3 \arrow[u] &
\end{tikzcd} \tag{3}$$

Crystals of **4** that are suitable for X-ray diffraction grow from hot tetrahydrofuran, and we used such crystals to determine the structure of **4**. (We submitted a preliminary report of this structure in ref 7.) A drawing of the structure is given in Figure 3.

Compound **4** is the cluster $(Et_3P)_6Co_6Te_8$. The six Co atoms form a slightly distorted octahedron (Co–Co distance approximately 3.23 Å). A Te atom caps each face of the octahedron thereby forming a concentric cube (Te–Te distance approximately 3.48 Å). The molecular structure is completed by the coordination of a single phosphine to each Co.

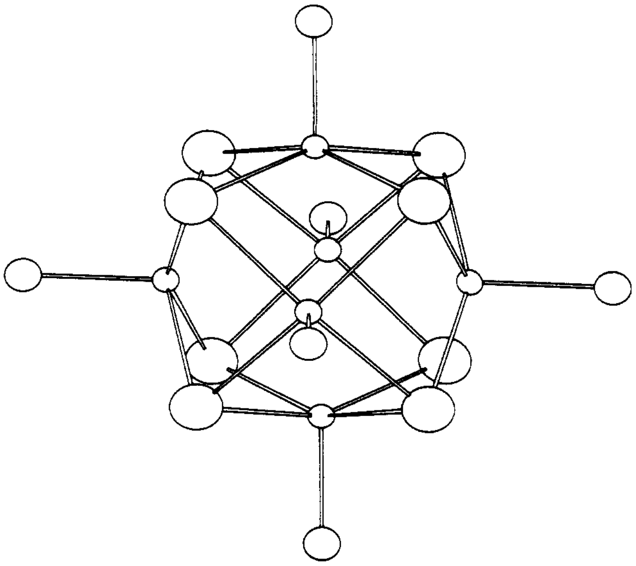

**Figure 3.** Drawing of the structure of $(Et_3P)_6Co_6Te_8$ (**4**). The large circles represent Te atoms, the small circles represent Co atoms, and the intermediate-sized circles represent P atoms. The ethyl groups are omitted for clarity. More complete details of this structure are included in ref 7.

The Co–Te bond lengths in **4** are between 2.51 and 2.53 Å. This is shorter than the Co–Te distances in **1**, **2**, and solid CoTe. This, together with the significantly shorter Co–P distance in **4** than in **1** and **2**, is consistent with a higher Co oxidation state in **4**. Similar $Co_6S_8$[8] and $Co_6Se_8$[9] cluster compounds have been reported in the literature.

**(D) Thermolysis of $(Et_3P)_6Co_6Te_8$ To Give β-CoTe.** In ref 7 we described the thermal behavior of **4**. We found that heating **4** in an evacuated, sealed tube results in the evolution of $Et_3P$ and the formation of β-CoTe (eq 4). The solid-state product was

$$(Et_3P)_6Co_6Te_8 \rightarrow \beta\text{-CoTe} + Et_3P \tag{4}$$

characterized[7] by powder X-ray diffraction and elemental analysis. The former showed diffraction due only to β-CoTe. (β-CoTe is a nonstoichiometric phase, $CoTe_x$, reported to occur between $x$ = 1.2 and $x$ = 1.8.[1]) The latter showed small amounts (<1%) of carbon, hydrogen, and phosphorus contamination and a Co/Te atomic ratio of 0.77. The Co/Te ratio is slightly higher than the input value of 0.75. We conjecture that the discrepancy is due to the removal of a small amount of Te by vapor transport by $PEt_3$ in the reaction tube.[10]

## Experimental Section

**General Methods.** Unless noted to the contrary all operations were carried out under an inert atmosphere using standard drybox and Schlenk techniques. All solvents were anhydrous grade, used as purchased from Aldrich. Dicobalt octacarbonyl (Alfa), triethylphosphine (Aldrich), and elemental tellurium (Alfa) were used without further purification. Triethylphosphine telluride was prepared by the action of triethylphosphine on tellurium as described in the literature.[11] NMR spectra were recorded using JEOL FX-90Q, GE QE-300, and Brucker AM-360 spectrometers. UV–visible absorption spectra were recorded on a Hewlett-Packard 8451a single-beam spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1320 spectrometer. The description of the thermolysis of **4** and the analysis of the solid-state product are included in ref 7.

Crystallographic data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation, using the NRCCAD program package. All subsequent calculations were performed on a MicroVAX II computer using the NRCVAX crystal structure system.[12] Gaussian integration absorption corrections were applied.

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(6) (a) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904. (b) Wei, C. H.; Dahl, L. F. *Cryst. Struct. Commun.* **1975**, *4*, 583.

(7) Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 2256.

(8) (a) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Polyhedron* **1985**, *5*, 2021. (b) Diana, E.; Gervasio, G.; Rossetti, R.; Valdermarin, F.; Bor, G.; Stranghellini, P. L. *Inorg. Chem.* **1991**, *30*, 294.

(9) Fenske, D.; Ohmer, J.; Hachengenei, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 993.

(10) Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245.

(11) Zingaro, R. A.; Stevens, B. H.; Irgolic, K. *J. Organomet. Chem.* **1965**, *4*, 320.

Refinement procedures were described elsewhere.[13] Hydrogen atoms were not included. Final positional and thermal parameters are included as supplementary material.

**Preparation of $[(Et_3P)_2(CO)_2CoTe]_2$.** $Co_2(CO)_8$ (0.42 g, 1.2 mmol), $Et_3PTe$ (0.6 g, 2.4 mmol), and $Et_3P$ (0.4 mL, 2.7 mmol) were combined in toluene (10 mL) at room temperature. Vigorous frothing resulted from the evolution of carbon monoxide. The mixture was stirred magnetically overnight, after which time it was heated (90–100 °C) for 1 h. The mixture was cooled back to room temperature, and the volatile components were removed in vacuo. The resulting dark solid was extracted with toluene (15 mL) and filtered. Heptane (20 mL) was added to the extract, and the solution was cooled to 0 °C. This gave a first crop (0.22 g) of crystalline solid. Further cooling to −30 °C gave an additional 0.29 g (total yield = 0.51 g = 0.51 mmol; 42%). The solid forms as deep emerald green crystals, which redissolve in toluene, benzene, tetrahydrofuran, and heptane to give yellow-brown solutions. Crystallization from toluene/heptane gives $(Et_3P)_4(CO)_4Co_2Te_2\cdot{}^1/_2$(toluene). Crystallization from tetrahydrofuran/heptane avoids the included solvent of crystallization.

UV–visible (toluene solvent): $\lambda_{max}$ = 310, 376 nm, unresolved shoulder at approximately 430 nm. IR (heptane; carbonyl region): 1945 (s), 1895 $cm^{-1}$ (s). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): 46.9 ppm downfield from (external) 85% $H_3PO_4$, $\Delta\nu_{1/2}$ = 16 Hz. $^1H$ NMR (benzene-$d_6$): $\delta$ 1.13 (m, 3 H), 2.32 (m, 2 H). Mp: 137–138 °C. Anal. Found (crystallized from tetrahydrofuran/heptane): C, 35.07; H, 6.18; Co, 12.20; P, 13.18; Te, 26.55. Calcd for $(Et_3P)_4(CO)_4Co_2Te_2$: C, 35.11; H, 6.31; Co, 12.31; P, 12.94; Te, 26.65. Found: (crystallized from toluene/heptane): C, 37.80; H, 6.27; Co, 11.80; P, 12.63; Te, 25.15. Calcd for $(Et_3P)_4(CO)_4Co_2Te_2\cdot{}^1/_2C_7H_8$: C, 37.69; H, 6.43; Co, 11.74; P, 12.34; Te, 25.42.

**Preparation of $(Et_3P)_4(CO)_6Co_4Te_2$. (a) From $[(Et_3P)_2(CO)_2CoTe]_2$.** A Schlenk tube was charged with **1** (250 mg, 0.26 mmol) and toluene (5 mL). $Co_2(CO)_8$ (90 mg, 0.26 mmol) and $Et_3P$ (0.3 mL) were added, followed by more toluene (5 mL). This gave a homogeneous, very dark yellow-brown solution. The mixture was heated at reflux approximately 1 h. Soon after the reflux temperature was reached the color of the mixture changed to very dark black-red. The solution remained homogeneous throughout. The mixture was cooled to room temperature, and the volatile components were removed in vacuo. The resulting solid was washed (4 × 5 mL of pentane) and dried in vacuo. The product was crystallized from warm toluene/heptane (10 mL of a 1:3 mixture, cooled to −30 °C). After crystallization was complete the supernatant liquor (still intensely colored) was decanted and the solid was washed (5 mL of pentane) and dried. This gave **2** (200 mg, 0.18 mmol; 68%). This material is identical to that made from cobalt carbonyl directly.

**(b) From $Co_2(CO)_8$ and $Et_3PTe$.** Elemental tellurium (0.37 g, 2.9 mmol) was suspended in toluene (20 mL) and treated with $Et_3P$ (2.2 mL, 14.9 mmol). When the Te had all dissolved, $Co_2(CO)_8$ (1.0 g, 2.9 mmol) was added directly as a solid. This gave frothing as the CO evolved. The resulting mixture was heated to reflux under argon for approximately 1 h. (During this time the reaction mixture changed in color from deep orange to very dark black-red.) The mixture was cooled to room temperature and reduced in volume to approximately 15 mL by evaporation in vacuo and filtered. Heptane (20 mL) was added, and the mixture was cooled to 0 °C. After several days $(Et_3P)_4(CO)_6Co_4Te_2$ formed as a black crystalline solid (1.09 g, 0.96 mmol, 66% based on $Co_2(CO)_8$). The compound is quite soluble in toluene and tetrahydrofuran and slightly soluble in heptane.

UV–visible absorption (toluene): $\lambda_{max}$ ($\epsilon$) = 316 (29 500), shoulder at 350 (approximately 20 000), 446 (11 000), barely resolved feature at 510 (7600), 556 (8000), 650 nm (5500). IR (heptane, carbonyl region): 1912 (s), 1770 $cm^{-1}$ (s). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): 35.0 downfield from (external) 85% $H_3PO_4$; $\Delta\nu_{1/2}$ = 540 Hz. This compound decomposes without melting. Anal. Found: C, 32.02; H, 5.47; Co, 19.21; P, 10.84; Te, 23.52. Calcd for $(Et_3P)_4(CO)_6Co_4Te_2$: C, 31.84; H, 5.34; Co, 20.83; P, 10.95; Te, 22.55.

**Preparation of $(Et_3P)_6Co_6Te_8$. (a) From $(Et_3P)_4(CO)_6Co_4Te_2$.** Compound **2** (0.59 g, 0.52 mmol), $Et_3PTe$ (0.42 g, 1.7 mmol), and $Et_3P$ (1.0 mL, 6.8 mmol) were combined in toluene (10 mL). This gave a homogeneous solution that was the black-red color characteristic of **2**. The mixture was heated at reflux for 2 h, during which time its color changed to a very deep cherry red. After the mixture was cooled to room temperature it was filtered through a medium-porosity glass frit to remove a small quantity of black solid. The solution was evaporated to dryness to give a dark solid (0.58 g). The UV–visible absorption spectrum of this material showed the $Co_6Te_8$ cluster (see below), and the IR spectrum showed a small amount of the CO-substituted $Co_6Te_8$ cluster. The residual CO was replaced by $PEt_3$ as follows: The crude solid (0.58 g) and $PEt_3$ (1.0 mL) were combined in toluene (10 mL), and the solution was heated at reflux for 7 h. The mixture was cooled to room temperature at which point crystallization commenced. Heptane (10 mL) was added, and the mixture was cooled to −30 °C. After crystallization was complete the supernatant liquor was decanted and the solid was washed (5 mL of pentane) and dried in vacuo. This gave $(Et_3P)_6Co_6Te_8$ (0.46 g, 0.22 mmol; 63%). The infrared spectrum of this material showed only a very small absorption due to residual CO. Independent tests (see below) show that prolonged heating in the presence of $PEt_3$ removes the CO completely. The analysis of this product is identical to that of the material prepared from $Co_2(CO)_8$ and $Et_3PTe$ directly.

**(b) From $Co_2(CO)_8$ and $Et_3PTe$.** $Co_2(CO)_8$ (2.06 g, 6.0 mmol) was dissolved in toluene (40 mL) and treated with $PEt_3$ (4 mL, 27 mmol) and $Et_3PTe$ (4.12 g, 16.8 mmol). The mixture was heated at reflux 2 h, after which time it was cooled to room temperature and filtered. The deep red solution was concentrated in vacuo, and pentane was added. Crystallization at −20 °C gave 2.60 g of a dark solid. The infrared spectrum of this material showed a small amount of (terminal) CO remaining. This was replaced with $Et_3P$ as described in part a above (reflux time 17 h). Subsequent crystallization gave **4** as a very dark crystalline solid.

UV–visible absorption (toluene): $\lambda_{max}$ ($\epsilon$) 398 (37 000), 474 (23 700), 538 nm (20 000). Infrared absorption ($CS_2$): the residual CO band is at 1930 $cm^{-1}$; other than that the IR shows only coordinated $Et_3P$. $^{31}P$-$\{^1H\}$ NMR (benzene-$d_6$): 88.1 ppm downfield from (external) 85% $H_3PO_4$, $\Delta\nu_{1/2}$ = 710 Hz. This compound decomposes without melting. Anal. Found: C, 20.86; H, 4.23; Co, 17.10; P, 8.74; Te, 49.00. Calcd for $(Et_3P)_6Co_6Te_8$: C, 20.75; H, 4.35; Co, 16.97; P, 8.92; Te, 49.00.

## Discussion

In earlier work we described mild, molecule-based syntheses of the known inorganic solid-state compounds MnTe,[2] $FeTe_x$[14] ($x$ = 1, 2), NiTe,[15] and PdTe.[16] Each of these syntheses has used the reaction of a trialkylphosphine telluride with an organometallic complex of the subject transition metal. By using milder reaction conditions in each case, we have been able to intercept molecular metal/tellurium complexes that can be converted to the solid-state compounds under the more vigorous conditions. In this sense the molecular complexes are intermediates in the molecules-to-solids processes. In the particular cases of Mn and Fe the intermediates are simple molecules that bear little resemblance to the final solid-state product. In the cases of Ni and Pd, on the other hand, the intermediates can be identified as small (albeit reconstructed) fragments of the growing solid-state crystal.

We chose to examine the reactions of $Co_2(CO)_8$ with $Et_3PTe$ as a complement to our earlier studies. Some of the questions we intended to answer in this work are as follows: (1) Can the solid cobalt telluride be prepared from these reagents? (2) Can intermediates be intercepted, characterized, and carried on to the solid product? (3) Are the intercepted intermediates simply small molecules (as in the Mn and Fe examples) or polynuclear clusters (as in the Ni and Pd examples)? (4) Can the structures of any or all of the isolated intermediates be rationalized in terms of the structure of the solid?

The reaction of $Co_2(CO)_8$ with 2 equiv of $Et_3PTe$ and 2 equiv of $Et_3P$ gives the dicobalt ditelluride **1**. The relative stoichiometry of the reagents and the length of the reaction time are important variables in this process. Prolonged heating gives $L_6Co_6Te_8$ (**3**) (L = $Et_3P$, CO), while either a deficiency of $Et_3PTe$ or a large excess of $Et_3P$ gives $L_{10}Co_4Te_2$ (**2**). We routinely conduct the reaction in toluene, but benzene and tetrahydrofuran give similar results. We realize the highest yield of **1** if the assembled reaction mixture is stirred at room temperature overnight before it is heated. (We have not studied this aspect of the process in any detail, but

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[12] (a) LePage, J.; White, P. S.; Gabe, E. J. *Proceedings of the American Crystallographic Association Annual Meeting of 1986*; Hamilton, Canada; AIP: New York, 1986; Poster PA23. (b) Gabe, E. J.; Lee, F. L.; LePage, J. In *Crystallographic Computing 3*; Sheldrick, G. H., Kruger, C., Goddard, R., Eds.; Clarendon: Oxford, England, 1985; p 163.

[13] Siegrist, T.; Schneemeyer, L.; Sunshine, S. A.; Waszczak, J. V. *Mater. Res. Bull.* **1988**, *23*, 1429.

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[16] Brennan, J. G.; Siegrist, T.; Stuczynski, S. M.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1990**, *112*, 9233.

the room-temperature reaction interval presumably permits the substitution of phosphine for CO to go to completion[17] in advance of the Co–Te bond forming steps.) The color of the reaction mixture does not change until the mixture is heated. During the heating, the color changes quickly from orange to dark brown. This leads us to believe that the Co–Te bond forming occurs only at elevated temperature.

Compound **1** crystallizes from toluene/heptane as large green cubes. The crystallization can be quite slow, occasionally taking several weeks. This accounts in part for the low yields of the isolated product.

The dicobalt ditelluride is our third example of a dimetal ditelluride,[2,12] each having been isolated from the reaction of $Et_3PTe$ with a metal–metal-bonded compound. Compound **1** and the dimanganese ditelluride $[(Et_3P)_2(CO)_3MnTe]_2$ (**5**) are particularly close relatives. One noteworthy structural distinction between the two is in the metal–tellurium bond distances. The Co–Te bond in **1** is shorter than the Mn–Te bond in **5** (2.614 Å versus 2.718 Å). This is consistent with the relative sizes of Co and Mn. The Co–Te distance in **1** is quite close to that in CoTe (2.614 Å versus 2.619 Å); however, the Mn–Te distance in **5** is markedly shorter[18] than that in MnTe (2.718 Å versus 2.921 Å). Presumably the difference in the Mn–Te distances is due to the change in the local electronic configuration at Mn. In **5** the Mn is low-spin $d^6$, while in MnTe[19] the Mn is high-spin $d^5$. This change accounts for the longer bond in the latter case.

In our work on organoiron tellurides we found that $Et_3P$ extracts a single Te atom from $[Cp(CO)(Et_3P)FeTe]_2$ (**6**) to give $[Cp(CO)(Et_3P)Fe]_2Te$ (**7**). The latter can be scavenged by added $[Cp(CO)_2Fe]_2$ and $Et_3P$ to give complete conversion of **6** to **7**. The analogous reaction of **1** with $Co_2(CO)_8$ and excess $Et_3P$ results in a related but distinctly different product $(Et_3P)_4(CO)_6Co_4Te_2$ (**2**).

Using the Fe–Te case as a guide, we can rationalize the formation and structure of **2** in the following way. The dicobalt ditelluride reacts with $Et_3P$ to give the (unobserved) monomeric dicobalt monotelluride $[(Et_3P)_2(CO)_2Co]_2Te$. The loss of phosphine from each Co and conversion of one of the CO ligands from the terminal mode to the bridging mode with the loss of another CO ligand would yield the hypothetical monomer $(Et_3P)_2(CO)_3Co_2Te$ (**8**). Dimerization of **8** via the bridging Te atoms would give the observed $Co_2Te_2$ complex. Given this description, in the same way that compound **1** can be appreciated as the dimer of the (CoTe) unit **2** can be appreciated as the dimer of the (CoTeCo) unit.

An alternative rationalization of **2** is predicated on the homolytic cleavage of the Te–Te bond in **1**. This bond breaking would give the Te-centered radical monomer $(Et_3P)_2(CO)_2CoTe$, which could react with cobalt carbonyl to give the Co–Te–Co linkage. Ligand reorganization, assisted by the excess of free phosphine in the system, would give **8** and the dimer, **2**, as above. This picture for the formation of **2** also marks **1** and **2** as the dimers of (CoTe) and (CoTeCo), respectively; however, it also emphasizes that the conversion of **1** to **2** is a growth reaction in which the CoTe moiety reacts with added Co to give the $Co_2Te$ moiety.

While the structure of **2** and that of $Co_4Te_2(CO)_{10}$ reported by Dahl and co-workers are quite similar, there is at least one notable difference. The unbridged Co–Co distance in **2** is longer than the corresponding distance in $Co_4Te_2(CO)_{10}$ (2.99 Å versus 2.88 Å). At the same time the CO-bridged Co–Co distances are the same (2.58 Å) in the two compounds. The steric repulsions between the vicinal phosphines has far more effect on the unbridged Co–Co "bond" than on the bridged. We cite this as evidence that **2** is a dimer of the $Co_2Te$ moiety and that the dimer bonding is via the Te bridges with no bonding between the unbridged Co–Co pairs.

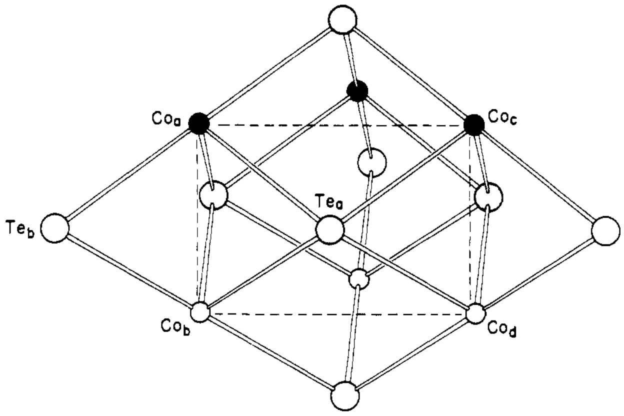

**Figure 4.** Fragment of the CoTe crystal structure. The large circles represent Te atoms, and the small circles represent Co atoms. This is the $Co_6Te_8$ fragment centered at $(a/2, a/2\sqrt{3}, c/4)$. The dashed lines connect the four Co atoms we associated with the $Co_4$ core of **2** (see Figure 5). The seven shaded atoms comprise the $Co_3Te_4$ unit shown isolated in Figure 6.

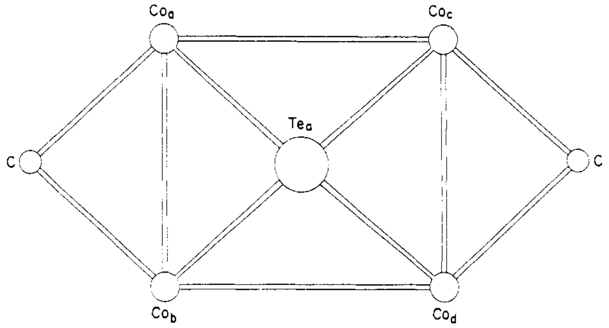

**Figure 5.** $Co_4(\mu_2\text{-}CO)_2Te$ fragment of **2**, as viewed from above the Te atom.

In the CoTe solid there are two fundamental Co–Co distances. The Co–Co distance in the *ab* plane is equal to $a$ (=3.893 Å in the stoichiometric solid), and the Co–Co distance along the $c$ direction is given by $c/2$ (=2.687 Å). The deviation of the $c/a$ ratio in CoTe from the NiAs ideal (1.381 versus 1.633) has been attributed to Co–Co bonding along the $c$ direction.[20] Structure **2** also shows two fundamental Co–Co distances: the CO-bridged (approximately 2.56 Å) and the unbridged (2.99 Å). The insensitivity of the former length and sensitivity of the latter to phosphine substitution at Co hints the presence and absence of metal–metal bonding in the respective situations.

This motivates the association of the CO-bridged Co–Co bond in **2** with the Co–Co interaction along the $c$ direction in solid CoTe and the association of the unbridged Co–Co geometry in **2** with the nonbonding Co–Co disposition in the *ab* plane in CoTe. The resulting correspondence between the structure of **2** and that of CoTe is shown explicitly in Figures 4 and 5. Figure 4 shows a fragment of the CoTe structure. A $Co_4$ unit is highlighted; this corresponding to $Co_4$ in **2**. In Figure 5 we show $Co_4$, the two $\mu_2$-CO ligands, and one of the Te atoms of **2**. It is interesting that the close Co pairs ($Co_a$–$Co_b$ and $Co_c$–$Co_d$) in CoTe are triply bridged, as are the close, CO-bridged Co pairs in **2**. Similarly the more remote pairs in CoTe ($Co_a$–$Co_c$ and $Co_b$–$Co_d$) are only doubly bridged, as are the "unbridged" pairs in **2**. The $Co_a$–$Te_a$–$Co_b$ angle in CoTe is 61.7° fairly close to the corresponding value of 60.6° in **2**.

Comparison of Figures 4 and 5 also shows the differences between **2** and CoTe. The four Co atom rectangle in **2** is spanned (essentially) symmetrically by two $\mu_4$-Te atoms. The corresponding rectangle in Figure 4 is spanned by only one such Te atom. The "unbridged" Co–Te–Co angle in **2** (71.5°) is much

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[17] See, for example: Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1.

[18] For NiAs type solids the A–B distance is given by $[(a^2/3) + (c^2/16)]^{1/2}$. For MnTe $a$ = 4.1429 Å and $c$ = 6.7031 Å. (See ref 18, p 249. See also JCPDS file No. 18-814).

[19] Furdyna, J. K. *J. Appl. Phys.* **1988**, *64*, R29.

[20] West, A. R. *Solid State Chemistry and Its Applications*; John Wiley & Sons: Chichester, U.K., 1984; Chapter 7.

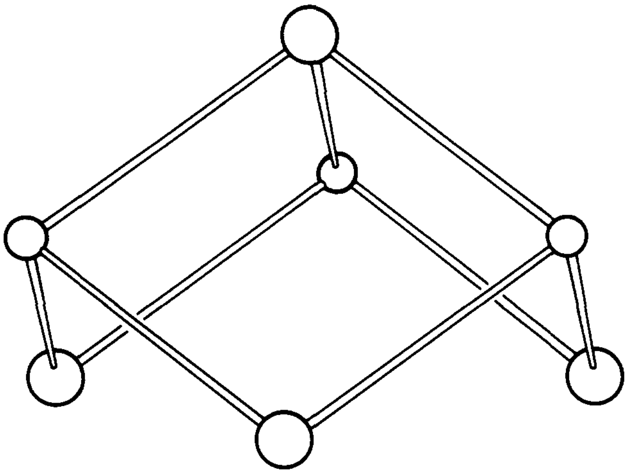

**Figure 6.** $Co_3Te_4$ fragment of the CoTe crystal. Symmetric dimerization of this unit gives a $Co_6$ octahedron concentric with a $Te_8$ cube.

smaller than the corresponding angle ($Co_a$–$Te_a$–$Co_c$ = 96°) in CoTe. The Te–Te distance in **2** (3.25 Å) is quite different from the Te–Te distance in CoTe (3.893 Å), and the nonbonding Co–Co distance in **2** (2.99 Å) is substantially at variance with the corresponding distance of 3.893 Å in CoTe. The structural differences can all be rationalized if **2** is appreciated as the dimer of $TeCo_2(\mu_2\text{-CO})$ (ignoring the other two-electron ligands). The distances and angles within the monomer agree well with the associated values in CoTe. The dramatic differences appear only in how the two monomers are fused to give the dimer. These structural correlations lead to the suggestion that bulk CoTe be viewed as a polymer of the $Co_a$–$Te_a$–$Co_b$–$Te_b$ nonplanar four-membered ring.

The structural analogy between **2** and solid CoTe would be more obvious were the $\mu_2$-CO ligands in **2** replaced with $\mu_2$-Te ligands. We tried to replace the $\mu_2$-CO ligands with Te by treating **2** with $Et_3PTe$; however, we have yet to see evidence for the formations of the (hypothetical) $\mu$-CO/Te exchange product, $(Et_3P)_4(CO)_4Co_4Te_4$. Instead, addition of phosphine telluride to the dicobalt monotelluride gives the cluster compound $(Et_3P)_6Co_6Te_8$ (**4**). When the correct stoichiometry is employed, **4** can be made from **2** in good yield.

We recently reported the synthesis of **4** directly from $Co_2(CO)_8$ and $Et_3PTe$ and the crystallographic determination of its structure. In that paper we showed that the $Co_6Te_8$ core of **4** is an identifiable, reconstructed fragment of crystalline CoTe. The void site in the CoTe structure (NiAs structure type) is defined by a triangular prism of six Co atoms and their eight shared Te neighbors (stoichiometry $Co_6Te_8$). Reconstruction of the triangular prism to an octahedron by 60° rotation of one of the triangular faces of the prism about the axis normal to the face (the *c* direction in the solid) followed by symmetrization of the Te sites gives the core geometry of **4**.

The structure of **4** can be reconciled with that of bulk CoTe in an alternate yet closely related way. The aforementioned void site in CoTe is shown in Figure 4. The $Co_3Te_4$ in Figure 6 is a closely packed stoichiometric half of that site. The symmetrical dimerization of this $Co_3Te_4$ would result in the core we see (Figure 3). In this sense **1** is the dimer of CoTe, **2** is the dimer of $Co_2Te$, and **4** is the dimer of $Co_3Te_4$. (It is interesting to note that the symmetrical dimerization of an $Mo_3S_4$ species has been used directly to prepare $(Et_3P)_6Mo_6S_8$—a cluster with which **4** is isostructural.[21]

There are some significant metrical differences between $Co_6Te_8$ in **4** and CoTe. The Co–Te bond length is 3.5% shorter in **4**. This, in conjunction with the reorganization of the Te coordination, gives a much shorter Te–Te distance in **4** (3.48 Å versus 3.893 Å in CoTe). The Co–Co distance in **4** (3.23 Å) is intermediate between the two values seen in CoTe (2.687 and 3.893 Å). These facts can be summarized by noting that the $Co_6Te_8$ unit is more closely packed in **4** than in CoTe. (The distance from the center of **4** to the Co atoms is 2.28 Å compared to the analogous distance in CoTe of 2.62 Å. The Te atoms in **4** are 3.01 Å from the molecular center; the corresponding eight Te atoms in CoTe are at 2.69 Å (2 Te), 2.97 Å (3 Te), and 4.50 Å (3 Te) from the void center.) It is easy to rationalize the more dense packing of **4** vis-a-vis the bulk solid. In CoTe the remainder of the solid exerts an outward force on the $Co_6Te_8$ unit that is absent in **4**. The molecular $Co_6Te_8$ can therefore relax to the more closely packed, more (internally) bonding structure we see in **4**.

## Conclusion

In this work we have identified three molecular compounds, **1**, **2**, and **4**, that result from the reaction of $Co_2(CO)_8$, $TePEt_3$, and $PEt_3$ in varying stoichiometries. These compounds are intermediates in a molecule-based synthesis of $\beta$-CoTe in the sense that when the same reagents are combined under more forcing conditions the extended solid compound forms.[7]

We have also shown that addition of $Co_2(CO)_8$ feedstock to **1** gives **2** and that addition of $TePEt_3$ feedstock to **2** gives **4**. In view of the relative molecular sizes these reactions can be considered growth processes.

We have also compared the structures of the molecular compounds with the ultimate solid-state product. We believe that since there are clear structural similarities, the molecular growth reactions may also be appreciated as the initial stages in the growth of the extended solid. The fact that there are also substantial differences between the molecular and solid structures is also interesting. It indicates, inter alia, that the ultimate NiAs-type structure of $\beta$-CoTe is not unequivocally established after just three growth steps. We are studying further reactions of **4** to determine when that point in the growth sequence is reached.

**Acknowledgment.** We gratefully acknowledge Paula Trevor for X-ray fluorescence measurements and G. Dabbaugh and E. Kwok for $^{31}P$ NMR measurements.

**Supplementary Material Available:** For the crystal structures of **1** and **2**, tables of crystallographic data, atomic coordinates, thermal parameters, and interatomic distances and angles (10 pages); tables of observed and calculated structure factors (67 pages). Ordering information is given on any current masthead page.

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(21) Saito, T.; Yamamoto, N.; Yamagata, T.; Imoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 1646.