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# The use of phosphine chalcogenides in the preparation of cobalt chalcogenides

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## Abstract

Dicobalt octacarbonyl reacts with $TeP^nBu_3$, $SeP^nBu_3$ or $SP^nBu_3$ to give solid state cobalt telluride, cobalt selenide and cobalt sulfide, respectively. In each case a cluster compound of the form $Co_6E_8(P^nBu_3)_6$ can be isolated from the reaction of the phosphine chalcogenide with cobalt carbonyl, and subsequently carried on to the solid state product. In this sense the $Co_6E_8$ clusters are intermediates in the molecules-to-solids processes. In the case of Se, another Co/Se cluster can be isolated: $Co_4Se_2(CO)_6(P^nBu_3)_4$. This complex also fits into the molecules-to-solids pathway inasmuch as it arises from $Co_2(CO)_8$ and $SeP^nBu_3$, and it is converted to the $Co_6Se_8$ cluster when treated with phosphine selenide.

These results show that molecules-to-solids pathways originally uncovered in studying reactions of $TePEt_3$ can be extended to other trialkylphosphines and other chalcogens.

## 1. Introduction

We have been studying reactions which lead from molecular reagents to extended inorganic solids [1,2]. One reason for this has been the utility of such reactions in technologically important processes such as Organometallic Vapor Phase Epitaxy (OMVPE) [1a–d,2]. A second reason has been the search for new ways to make nanoscale materials such as semiconductor clusters which demonstrate quantum confinement [1e–h,3]. A third reason has been to try to determine some of the pathways that are taken by the molecular reagents on their ways to the solid products [1i–k,2]. In several of our studies we have used trialkylphosphine tellurides as reactive sources of tellurium for the production of solid metal tellurides [1b,1i–k,2]. These reagents were chosen originally because of the early literature report that phosphine tellurides readily disproportionate at low temperatures to deposit elemental tellurium [4]. In our desire to extend this work to the higher phosphine chalcogenides we report now the reactions of phosphine selenides and phosphine sulfides with dicobalt octacarbonyl.

## 2. Experimental details

All manipulations were conducted under an inert atmosphere unless otherwise noted. Solvents were anhydrous grade, and these, as well as $PEt_3$ and $P^nBu_3$, were used as received from Aldrich. Dicobalt octacarbonyl and selenium were used as received from Alfa. Phosphine telluride, phosphine selenide and phosphine sulfide reagents were generated *in situ* by direct combination of the phosphine and chalcogen. NMR spectra were recorded in $d_8$-toluene on a GE QE-300 spectrometer. Infrared spectra were recorded in $CS_2$ on a Perkin-Elmer 683 spectrometer. UV-Visible absorption spectra were recorded in toluene on an HP 8451A spectrometer. Powder X-ray diffraction patterns were recorded using a Rigaku Miniflex diffractometer (Cu K$\alpha$ radiation).

### 2.1. *Preparation of* $Co_6Te_8(P^nBu_3)_6$

Dicobalt octacarbonyl (3.06 g, 9.0 mmole), $P^nBu_3$ (14.0 g, 69 mmole) and elemental Te (4.98 g, 39 mmole) were combined in toluene (60 ml), stirred at room temperature for 30 min and then heated at reflux for 20 h. The resulting mixture was cooled to room temperature, filtered and concentrated *in vacuo* to approximately 20 ml. Pentane (10 ml) was added and the

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solution was cooled to −20°C to initiate crystallization. After 18 h the supernatant liquor was decanted and the crystalline solid was washed (3 × 5 ml pentane) and dried *in vacuo* to give $Co_6Te_8(P^nBu_3)_6$ as a very dark red-black crystalline solid (5.84 g, 2.3 mmole, 77%). This compound is slightly air-sensitive. Analysis (Analytische Laboratorien), found (calculated for $C_{72}H_{162}Co_6P_6Te_8$: C, 33.34 (33.41); H, 6.19 (6.31); Co, 13.50 (13.66); P 7.24 (7.18); Te, 39.20 (39.44%). $^{31}P\{^1H\}$-NMR: 189.9 ppm downfield from (external) 10% $P(OCH_3)_3$; fwhm = 335 Hz. UV-Vis, $\lambda_{max}$ ($\epsilon$): 400 nm (60450), 476 nm (38350), 538 nm (32600). The infrared spectrum shows only coordinated $P^nBu_3$.

### 2.2. Preparation of $Co_6Se_8(P^nBu_3)_6$

Dicobalt octacarbonyl (1.03 g, 3.0 mmole), $P^nBu_3$ (2.63 g, 13 mmole) and elemental Se (1.03 g, 13 mmole) were combined in toluene (20 ml), stirred at room temperature 1 h and then heated at reflux for 1.5 h. The resulting mixture was cooled to room temperature, filtered and concentrated to approximately 10 ml, after which point it was cooled to −20°C. After crystallization was complete (overnight) the supernatant liquor was decanted and the solid was washed with pentane (3 × 5 ml) and dried *in vacuo*. This gave $Co_6Se_8(P^nBu_3)_6$ (1.29 g, 0.59 mmole, 59%) as a very dark orange brown solid. This material is slightly air-sensitive. Analysis (Analytische Laboratorien), found (calculated for $C_{72}H_{162}Co_6P_6Se_8$): C, 39.50 (39.32); H, 7.27 (7.42); Co, 15.90 (16.08); P 8.44 (8.45); Se, 28.45 (28.72%). $^{31}P\{^1H\}$-NMR: 161.5 ppm downfield from (external) 10% $P(OCH_3)_3$; fwhm = 462 Hz. UV-Vis, $\lambda_{max}$ ($\epsilon$): 370 nm (60710), 442 (43080), 498 nm (25070). The infrared spectrum shows only coordinated $P^nBu_3$.

### 2.3. Preparation of $Co_6S_8(P^nBu_3)_6$

Dicobalt octacarbonyl (1.03 g, 3.0 mmole), $P^nBu_3$ (2.63 g, 13 mmole) and elemental S (0.42 g, 13 mmole) were combined in toluene (20 ml), stirred at room temperature for 30 min and then heated at reflux for 1.5 h. At the end of this time the mixture was cooled to room temperature and the solvent was removed *in vacuo* and replaced with $Et_2O$ (10 ml). The mixture was warmed slightly and then cooled to −20°C overnight to give crystallization. The supernatant liquor was decanted and the product was washed with cold ether (3 × 5 ml) and dried *in vacuo*. This gave $Co_6S_8(P^nBu_3)_6$ as a very dark orange solid (0.34 g, 0.19 mmole, 19%). This compound is very soluble in common organic solvents and is air-sensitive. Analysis (Analytische Laboratorien), found (calculated for $C_{72}H_{162}Co_6P_6S_8$: C, 47.67 (47.41); H, 9.09 (8.95); Co, 19.10 (19.39); P 10.27 (10.19); S, 13.88 (14.06%). $^{31}P\{^1H\}$-NMR: 147.8 ppm downfield from (external) 10% $P(OCH_3)_3$; fwhm = 400 Hz. UV-Vis, $\lambda_{max}$ ($\epsilon$): 342 nm (68020), 416 nm (49410), 474 nm (23730). The infrared spectrum shows only coordinated $P^nBu_3$.

### 2.4. Preparation of $Co_4Se_2(CO)_6(P^nBu_3)_4$

Dicobalt octacarbonyl (1.03 g, 3.0 mmole), $P^nBu_3$ (2.43 g, 12.4 mmole) and elemental Se (0.238 g, 3.01 mmole) were combined in toluene (30 ml), heated at reflux for 2.5 h, cooled to room temperature and filtered. The resulting solution was evaporated *in vacuo* to give a densely colored oil. Pentane (3 ml) was added and the resulting solution was cooled to −20°C for several days to give crystallization. The supernatant liquor was decanted and the residue was washed with cold pentane and dried to give $Co_4Se_2(CO)_6(PEt_3)_4$ (1.09 g, 0.80 mmole, 53%) as a dark green crystalline solid. This compound is slightly air-sensitive. Analysis (Analytische Laboratorien), found (calculated for $C_{54}H_{108}Co_4O_6P_4Se_2$: C, 47.14 (47.31); H, 7.83 (7.94); Co, 17.10 (17.19); P 9.24 (9.04); Se, 11.35 (11.52%). UV-Vis, $\lambda_{max}$ ($\epsilon$): 367 nm (26030), 440 nm (19270), 542 nm (12580), 630 nm (11550). IR (heptane): 2039 w, 1932 s, 1892 w, 1784 s $cm^{-1}$.

### 2.5. Conversion of $Co_4Se_2(CO)_6(P^nBu_3)_4$ to $Co_6Se_8(P^nBu_3)_6$

$Co_4Se_2(CO)_6(P^nBu_3)_4$ (300 mg, 0.22 mmole) was dissolved in toluene (15 ml) and treated with $P^nBu_3$ (100 mg, 0.5 mmole) and Se powder (92 mg, 1.2 mmole). The resulting solution was heated at reflux approximately 2 h. During this time the originally greenish solution turned deep orange. The mixture was cooled to room temperature and filtered. The volatile components were removed *in vacuo* and the oil was extracted with pentane (5 ml). The extract was cooled to −20°C overnight. Isolation as above gave $Co_6Se_8(P^nBu_3)_6$ (190 mg, 0.087 mmole, 59%). This material is identical to that prepared directly from $Co_2(CO)_8$ and $SeP^nBu_3$.

### 2.6. Thermal conversion of $Co_6Te_8(P^nBu_3)_6$ to β-CoTe

$Co_6Te_8(P^nBu_3)_6$ (0.283 g, 0.109 mmole) was sealed in an evacuated pyrex tube and heated to 400°C for 1 h. This liberated $P^nBu_3$ and left a dark grey solid. The solid was collected, washed (pentane) and dried *in vacuo* (yield = 0.151 g, 100% recovery of Co and Te). Powder X-ray diffraction shows only β-CoTe [5].

### 2.7. Thermal conversion of $Co_6Se_8(P^nBu_3)_6$ to γ-CoSe

$Co_6Se_8(P^nBu_3)_6$ (81 mg, 0.037 mmole) was sealed in an evacuated pyrex tube and heated at 400°C for 100 min. This liberated the $P^nBu_3$ and left a dark gray solid. The solid was washed with pentane and dried (yield: 30 mg; complete recovery of just Co and Se would give 36 mg). Powder X-ray diffraction shows only γ-CoSe [6*].

### 2.8. *Thermal conversion of $Co_6S_8(P^nBu_3)_6$ to solid cobalt sulfide*

$Co_6S_8(P^nBu_3)_6$ (62 mg, 0.034 mmole) was sealed in an evacuated pyrex tube and heated at 400°C for approximately 2 h. As distinct from the Te and Se complexes, this material melted before forming the solid state product. The sample was cooled and the solid was collected, washed (2 × 2 ml pentane) and dried (yield: 19 mg; complete recovery of just Co and S would give 21 mg). Powder X-ray diffraction shows only peaks assigned to cobalt-rich CoS [7*].

## 3. Results

We examined the reaction of $Co_2(CO)_8$ with $SePEt_3$ in refluxing toluene and found the production of Co/Se molecular compounds to be too sluggish to be useful. We chose the alternative reagents $EP^nBu_3$ (E = chalcogen). To test the validity of this choice we allowed $Co_2(CO)_8$ to react with $TeP^nBu_3$. The two were combined under conditions identical to those used earlier to prepare $Co_6Te_8(PEt_3)_6$ [2], and we found that the analogous cluster compound, $Co_6Te_8(P^nBu_3)_6$ (**1**) is formed in good yield. Compound **1** is identified by $^{31}P$-NMR (as in the spectrum of $Co_6Te_8(PEt_3)_6$, a single broad resonance), UV-Visible absorption spectroscopy (three strong bands at room temperature, qualitatively identical to the $PEt_3$ case, Fig. 1) and elemental analysis. As in the case of $Co_6Te_8(PEt_3)_6$, compound **1** can be converted to β-CoTe thermally: differential scanning calorimetry of $Co_6Te_8(P^nBu_3)_6$ shows an endothermic peak at approximately 215°C which we assign to the dissociation of phosphine and formation of solid state cobalt telluride. We verified this by conducting the pyrolysis on a preparative scale.

In the same way the reaction of $Co_2(CO)_8$ with $SeP^nBu_3$ in an approximate 1:4 ratio in refluxing toluene gives $Co_6Se_8(P^nBu_3)_6$ (**2**). Compound **2** was identified by elemental analysis as well as its spectroscopic similarity to **1**. The $^{31}P$-NMR of **2** shows a single broad resonance 28.4 ppm upfield from that of **1**, and the UV-Visible absorption spectrum of **2** shows the three-band pattern that is characteristic of the $L_6Co_6Te_8$ complexes (Fig. 1). The infrared absorption spectrum of **2** shows the absence of CO ligands.

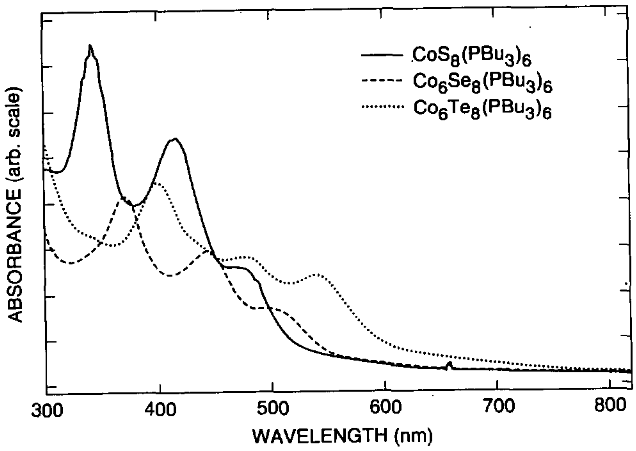

Fig. 1. UV-Visible absorption spectra of **1**, **2** and **4**, recorded in toluene solution. Extinction coefficients are listed in the text.

When $Co_2(CO)_8$ and $SeP^nBu_3$ are combined in refluxing toluene in a Co:Se atomic ratio of unity in the presence of additional $P^nBu_3$, the smaller cluster, $Co_4Se_2(CO)_6(P^nBu_3)_4$ (**3**) forms. Compound **3** is identified by elemental analysis, and by spectroscopic comparison to $Co_4Te_2(CO)_6(PEt_3)_4$ [2]. The infrared spectrum of **3** shows both terminal and bridging CO ligands, and the UV-Visible absorption spectrum of **3** shows four well-defined bands stretching across the visible. These spectra are both qualitatively quite similar to those of $Co_4Te_2(CO)_6(PEt_3)_4$. The addition of $SeP^nBu_3$ to **3** in warm toluene results in the formation of **2**. This is in direct analogy to our previous observation [2] that $Co_4Te_2(CO)_6(PEt_3)_4$ reacts with $TePEt_3$ to give $Co_6Te_8(PEt_3)_6$.

Differential scanning calorimetry of $Co_6Se_8(P^nBu_3)_6$ shows an endothermic peak at approximately 335°C which we assign to the dissociation of phosphine and formation of solid state cobalt selenides. To verify this we pyrolyzed **2** in the solid state in static vacuum at 400°C. The mass of the solid recovered from this pyrolysis was 83% of that expected from simple loss of phosphine and crystallization of the $Co_6Se_8$ cluster nuclei into solid cobalt selenides.

We also found that dicobalt octacarbonyl reacts with $SP^nBu_3$. When the two are combined in an approximate 1:4 ratio in refluxing toluene the hexanuclear cluster $Co_6S_8(P^nBu_3)_6$ (**4**) is formed, and can be isolated as a crystalline solid. Compound **4** is identified by comparison to the Te and Se analogues: $^{31}P$-NMR shows a single, broad peak 13.7 ppm upfield from that of $Co_6Se_8(P^nBu_3)_6$; infrared absorption spectroscopy shows the absence of Co; and UV-Visible absorption spectroscopy shows the three characteristic bands (Fig. 1).

The thermal behavior of **4** is similar to that of **2**. The DSC trace of **4** shows a set of endothermic peaks between 325°C and 350°C which we assign to the

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* Reference number with asterisk indicates a note in the list of references.

dissociation of phosphine and the formation of solid state cobalt sulfides. To verify this we similarly pyrolyzed **4** in the solid state in vacuum at 400°C. The mass of the solid recovered from this pyrolysis was 92% of that expected from simple loss of phosphine and condensation of the $Co_6S_8$ cluster nuclei.

## 4. Discussion

One strategy for the molecular precursor based preparation of extended inorganic solids is to combine zerovalent organometallic complexes of the various elements of interest. The resulting mixture is subjected to conditions under which the inorganic elements combine to form the solid while at the same time the organic ligands are liberated and removed. We have used this prescription (eqn. 1) to make several transition metal tellurides. In a heuristic sense one may view this synthesis method as a combination of "masked atoms". Phosphine chalcogenides are attractive for this use because the phosphorus-chalcogen bond is not a typical covalent bond. In the case of phosphine tellurides the phosphorus–tellurium interaction has been described as a simple phosphorus-to-tellurium donor accepted bond [8]. The reactivity of these compounds supports this description inasmuch as gentle heating of solutions of phosphine tellurides results in the cleavage of the P–Te bond and the deposition of elemental tellurium.

$$L_nM^{(0)} + R_3PTe^{(0)} \rightarrow \rightarrow \rightarrow M_xTe_y + nL + R_3P \qquad (1)$$

We are interested in determining the scope and limitations of the "combination of atoms" approach; and in particular in finding whether phosphine selenides and/or sulfides can be used for solid metal-chalcogenide materials synthesis. The primary question is whether or not the increased strength of the phosphorus–chalcogen bond precludes the formation of transition metal–chalcogen bonds. In our first report on this topic [9] we showed that $Et_3PSe$ reacts with $Ni^0$ complexes to give products, both molecular and solid state, that are not strictly analogous to those formed from $Et_3PTe$ and $Ni^0$.

We have studied the reactions of $Et_3PT_e$ with $Co_2(CO)_8$ in detail [2], and found that these reagents can be used to make solid state cobalt tellurides, and that at least three molecular intermediates can be intercepted from this process (eqns. 2–5). We have also shown that there are structural similarities (as well as differences) between the isolated cluster intermediates and the extended solid, and that as the clusters become larger the set of structural relationships with the extended solid becomes larger. For these reasons the cobalt chalcogenide systems are well suited for studying the reactions of phosphine selenides and phosphine sulfides in relation to those of phosphine tellurides.

$$Co_2(CO)_8 + 2\ TePEt_3 + PEt_3 \longrightarrow [(Et_3P)_2(CO)_2CoTe]_2 \qquad (2)$$

$$[(Et_3P)_2(CO)_2CoTe]_2 + Co_2(CO)_8 \longrightarrow Co_4Te_2(CO)_6(PEt_3)_4 \qquad (3)$$

$$Co_4Te_2(CO)_6(PEt_3)_4 + TePEt_3 \longrightarrow Co_6Te_8(PEt_3)_6 \qquad (4)$$

$$Co_6Te_8(PEt_3)_6 \longrightarrow Co_3Te_4 + PEt_3 \qquad (5)$$

Dicobalt octacarbonyl reacts with both $SePEt_3$ and $SPEt_3$ in refluxing toluene as evidenced by the change in color of the reaction solutions. In neither case was it possible for us to isolate $Co_6E_8(PEt_3)_6$ compounds, instead we recovered phosphine chalcogenide on attempted crystallization of the Co/E clusters. We attribute this to both the avidity with which the phosphine chalcogenide crystallizes and the intrinsic stability of the P–E bond. We aimed to disturb both of these effects and thereby promote the formation and isolation of Co/E cluster compounds by using $P^nBu_3$ in place of $PEt_3$ in these reactions.

Dicobalt octacarbonyl reacts with $TeP^nBu_3$, $SeP^nBu_3$ and $SP^nBu_3$ in refluxing toluene to form $Co_6Te_8(P^nBu_3)_8$ (**1**), $Co_6Se_8(P^nBu_3)_8$ (**2**) and $Co_6Se_8(P^nBu_3)_8$ (**4**) respectively. These reactions are more efficient when conducted with an excess of phosphine chalcogenide (this is in contrast to the reaction of $Co_2(CO)_8$ with $TePEt_3$ in which a starting Co : Te ratio of 6 : 8 gives $Co_6Te_8(PEt_3)_6$ in good yield). We speculate that this is due at least in part to the reactions being slower owing to the bulkier butyl substituents on the phosphine.

Compounds **1**, **2** and **4** crystallize well, albeit slowly, and as might be expected they are quite soluble in organic solvents. Infrared and NMR spectroscopies are helpful in assaying the purity of these compounds, but not in directly assigning molecular structures; the structures being assigned on the basis of spectroscopic comparison to $Co_6Te_8(PEt_3)_6$ (see above). The molecular structure of $Co_6Te_8(PEt_3)_6$ is shown in Fig. 2. It consists of an octahedron of Co atoms concentric with a cube of Te atoms, the structure being completed by a phosphine ligand on each Co atom. (For complete structural details, see ref. [2]). We infer that the structures of **1**, **2** and **3** are analogous. Compounds of the form $Co_6E_8L_6$ ($E = Se$, $L = PPh_3$ [10]; $E = S$, $L = PEt_3$ [11], $PPh_3$ [12], CO [13]) have been reported, prepared via different routes.

The UV-Visible absorption spectra of the three congeners (Fig. 1) show a clear trend. Each of the absorption bands shifts to progressively shorter wave-

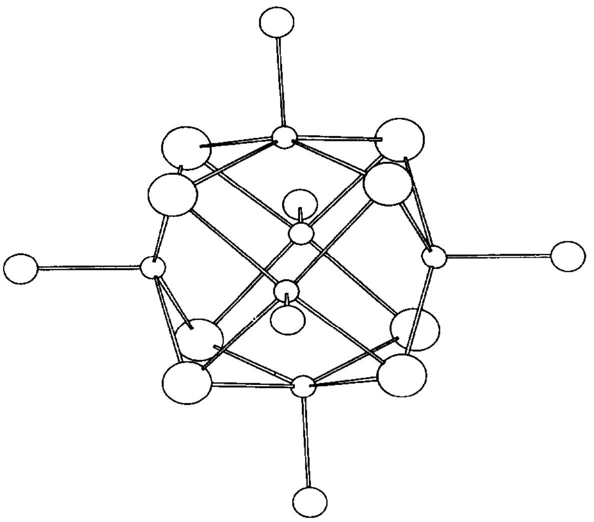

Fig. 2. The molecular structure of $Co_6Te_8(PEt_3)_6$. Large circles represent Te atoms, small circles Co atoms. Ethyl groups are not shown. A full discussion of this structure can be found in ref. 2.

length on going from Te to Se to S. This is presumably due to the increase in Co–E bond strength in the same sense. It is also expected that the excited states become more localized and therefore higher in energy on going from Te to Se to S.

As mentioned above we were able to intercept three molecular complexes between $Co_2(CO)_2$ plus $TePEt_3$ and solid β-CoTe, molecules having the heavy-atom stoichiometries $Co_2Te_2$, $Co_4Te_2$ and $Co_6Te_8$. In none of the present cases were we able to isolate $Co_2E_2$ complexes, however we were able to isolate the corresponding $Co_4Se_2$ complex and see evidence for the $Co_4S_2$ complex [14*]. The structure of the $Co_4Te_2(CO)_6(PEt_3)_4$ complex [from ref. 2] is shown in Fig. 3. It shows a rectangle of Co atoms capped above and below by Te. A number of compounds having this $Co_4E_2$ core have been reported in the literature [15]. We have assigned the analogous structure to **3** based on its spectroscopic similarity to $Co_4Te_2(CO)_6(PEt_3)_4$. As further evidence, **3** reacts with added phosphine selenide to give **2** just as the $Co_4Te_2$ complex reacts with added phosphine telluride to give the corresponding $Co_6Te_8$ cluster. In ref. 2 we described the structures of the several Co/Te clusters in terms of the ultimate CoTe extended solids and rationalized the molecule-to-molecule conversions as microscopic versions of solid state growth reactions. We suggest the same in the present case: the reaction of **3** with $SeP^nBu_3$ to give **2** may be viewed as an initial step in the growth of the Co/Se solid lattice.

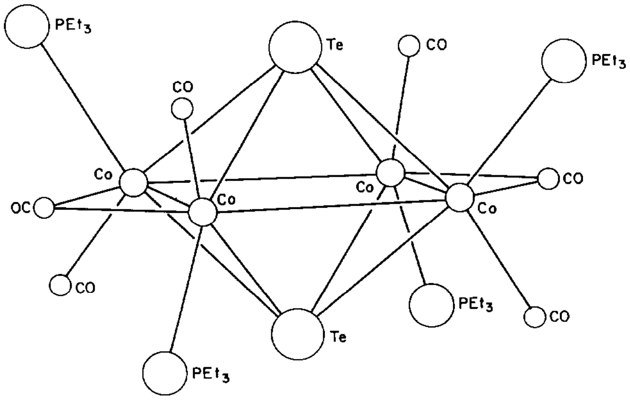

Fig. 3. The molecular structure of $Co_4Te_2(CO)_6(PEt_3)_4$. Large circles represent Te atoms, smaller circles Co atoms. A full discussion of this structure can be found in ref. 2.

Each of the $Co_6E_8$ cluster compounds can be converted to solid state cobalt chalcogenides. The DSC traces of the three are qualitatively similar: the features we believe correspond to the loss of phosphine and formation of the solids are all endothermic with the characteristic temperatures being approximately 215, 335 and 325–350°C for Te, Se and S, respectively. We rationalize this trend in terms of Co–P bond strengths. Since the Co–Te bonds are less polar than the Co–Se and Co–S bonds the Co centers in **1** are more electron-rich and therefore the Co–P bonds in **1** are expected to be weaker, hence the lower thermolysis temperature for **1**. Cluster **1** decomposes at a lower temperature than does $Co_6Te_8(PEt_3)_6$ (215 *versus* 260°C). We rationalize this on the basis of increased steric crowding at Co in the $P^nBu_3$ case. The solid product of the thermolysis of $Co_6S_8(P^nBu_3)_6$ is cobalt-rich (shown by X-ray diffraction). We believe that this is due to the removal of sulfur from the initial solid product by the liberated $P^nBu_3$ to give a small amount of $SP^nBu_3$. We have previously shown [1b] that trialkylphosphines can be effective chemical vapor transport agents for Te, and believe that the same phosphines can transport the lighter chalcogens as well.

## 5. Conclusion

In this work we have found that $Co_2(CO)_8$ reacts with $EP^nBu_3$, generated *in situ*, in essentially the same way as it does with $TePEt_3$. In each case the $Co_6E_8(P^nBu_3)_6$ cluster compound can be isolated as a crystalline solid which can then be carried on to the extended solid cobalt chalcogenides. The thermochemical trends encountered can be rationalized in terms of the simple differences among the chalcogens. This indicates that the "combination of atoms" approach to the design of molecules-to-solids processes can be extended in some cases from tellurium to the lighter chalcogens. This can all be contrasted with the reactions of $Ni^0$ with phosphine chalcogens in which different chalcogens give both different types of cluster intermediates and different types of extended solids.

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