

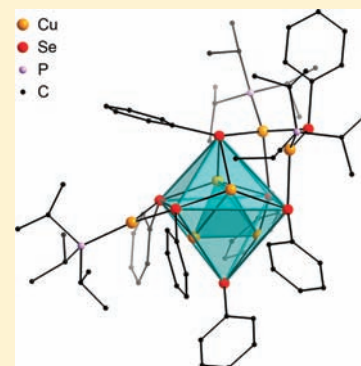
## Trialkylphosphine-Stabilized Copper(I) Phenylchalcogenolate Complexes - Crystal Structures and Copper–Chalcogenolate Bonding

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Supporting Information

**ABSTRACT:** A series of trialkylphosphine-stabilized copper(I) phenylchalcogenolate complexes  $[(R_3P)_m(CuEPh)_n]$  ( $R = Me, Et, ^iPr, ^tBu$ ;  $E = S, Se, Te$ ) has been prepared and structurally characterized by X-ray diffraction. Structures were found to be mono-, di-, tri-, tetra-, hexa-, hepta-, or decanuclear, depending mainly on size and amount of phosphine ligand. Several structural details were observed, including unusually long Cu–E bonds or secondary Cu–E connections,  $\mu_4$ -bridging, and planar bridging chalcogenolate ligands. Relatively rigid Cu–E–C angles were found to be of significant influence on the flexible molecular structures, especially for bridging chalcogenolate ligands, since in these cases a correlation results between the Cu–E–Cu angles and the inclination of the E–C bonds to their Cu–E–Cu planes. We further address some of these phenomena by means of density functional computations.



## INTRODUCTION

Usually, the motivation for investigations of metal chalcogenolates<sup>1</sup> is their importance in biological systems,<sup>2</sup> or their ability to act as precursor compounds in the generation of metal chalcogenides.<sup>3</sup> We use these binary compounds as starting materials of definite composition for the synthesis of ternary compounds. As it turned out, a big variety of compositions can be obtained, and secondary copper–chalcogen connections and extraordinarily long copper–chalcogen bonds occur in these molecules. Therefore, we decided to perform a systematic X-ray structural study in order to address this phenomena and explain the molecular structures in terms of steric and electronic factors with further information from quantum chemical calculations.

While copper(I) phenylthiolate forms polymeric chains, as shown in a recent X-ray powder diffraction study,<sup>4</sup> the structures of the homologous selenium and tellurium compounds are still unknown. Copper(I) phenylselenolate can be obtained as a brownish yellow precipitate from cuprous oxide and phenylselenol.<sup>5</sup> Without the support of strongly coordinating ligands (e.g., phosphines) several phenylchalcogenocuprates are accessible. The ion  $[Cu(SPh)_3]^{2-}$  was reported in two different conformations,<sup>6,7</sup> and coordination to a  $(CuSPh)_3$ -ring leads to the ion  $[Cu_4(SPh)_6]^{2-}$ , which is built up by a tetrahedral arrangement of trigonally coordinated copper atoms.<sup>6,8</sup> The homologous ion with selenium is also known and was found to exhibit the same structure.<sup>9</sup>

With triphenylphosphine as an additional ligand several neutral polynuclear complexes of the general formula  $[(Ph_3P)_m(CuEPh)_n]$  ( $E = S, Se$ ) are accessible. The dinuclear compounds  $[(Ph_3P)_4(CuSPh)_2]$ <sup>10</sup> and  $[(Ph_3P)_3(CuSePh)_2]$ <sup>11</sup> have been reported to form four-membered ring systems, the latter

containing trigonal planar as well as tetrahedrally coordinated copper atoms. The compound  $[(Ph_3P)_4(CuSPh)_3]$  forms a six-membered ring of alternating copper and sulfur atoms,<sup>12</sup> and  $[(Ph_3P)_4(CuSPh)_4]$  was described as a distorted step structure.<sup>13</sup> With diphenyl-ethyl-phosphine, the hexanuclear complex  $[(Ph_2EtP)_5(CuTePh)_6]$  could be obtained,<sup>14</sup> forming the same cage structure as the related silver compound  $[(Ph_3P)_5(AgSC_6H_4Cl)_6]$ .<sup>15</sup>

Some trialkylphosphine-stabilized copper–phenyltellurolates have already been reported,<sup>16</sup> namely,  $[(Me_3P)_4(CuTePh)_2]$  and  $[(^iPr_3P)_3(CuTePh)_4]$ , but while the report focused on the photolysis of these substances to obtain mixed tellurolate–telluride systems, we reinvestigated the structures of the tellurolates and avoided any photolysis. We extended the study to the lighter chalcogens sulfur and selenium, for which surprisingly no structures were reported before. The systematic use of  $Me_3P$ ,  $Et_3P$ ,  $^iPr_3P$ , and  $^tBu_3P$  allowed for determination of the sterical influence of the phosphine ligand, since they span a wide range of cone angles.<sup>17</sup>

## RESULTS AND DISCUSSION

**1. Crystal Structures.** Trialkylphosphine-stabilized copper(I) phenylchalcogenolate complexes of the general formula  $[(R_3P)_m(CuEPh)_n]$  ( $E = S, Se, Te$ ) can be obtained in high yield by the reaction of copper(I) acetate with the silylated phenylchalcogenolates under elimination of  $Me_3SiOAc$  in the presence of the appropriate amount of phosphine ligand

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(Scheme 1). Alternatively, cuprous oxide can be reacted with the phenylchalcogenol, which requires higher temperatures and at least 2 equiv of phosphine ligand. Complexes can be interconverted into each other by addition of phosphine ligands, increasing the ratio  $m/n$ , or by mixing with CuEPh (if accessible), decreasing the ratio  $m/n$ .

Table 1 gives an overview of the compounds we obtained. After a brief description of the overall molecular structures and noteworthy properties, a discussion of the structural parameters (e.g., bond lengths and angles) will be given in a comparative manner, focusing on unusual observations, supported by quantum chemical calculations to understand and explain some of the observed trends. Preparative and computational details as well as structural data are part of the Supporting Information, and

relevant crystallographic data and refinement details are given in Tables 2, 3, and 4.

By use of 3 equiv of triethylphosphine the copper atoms can be shielded sterically and saturated electronically, leading to mononuclear phenylchalcogenolates  $[(Et_3P)_3CuEPh]$  with E = S (**1**), Se (**2**), and Te (**3**). The structures are shown in Figure 1. These compounds melt between 15 and 20 °C, giving colorless oils at room temperature. The copper atoms display a distorted tetrahedral environment, with P–Cu–P angles somewhat larger than 109°. Cu–E distances are 235.75(7) pm for E = S, 247.74(7) pm for E = Se, and 268.9(2) pm for E = Te.

These compounds resemble the series  $[(Et_3P)_3CuESiMe_3]$ ,<sup>18</sup> the main differences are 2–5 pm shortened Cu–E bonds and about 10° smaller Cu–E–R angles (R = Ph, SiMe<sub>3</sub>) in **1–3** compared with the analogous trimethylsilylchalcogenolates. Both can be attributed to sterical reasons. A striking difference is the <sup>77</sup>Se-NMR shift, which is reported to be –570 ppm for  $[(Et_3P)_3CuSeSiMe_3]$  and is found to be +74 ppm for **2**.

If less than 1 equiv of triethylphosphine is used in the synthesis, the hexanuclear compounds  $[(Et_3P)_5(CuEPh)_6]$  (E = S (**4**), Se (**5**), and Te (**6**)) can be isolated. These structures are shown in Figure 2. The structure of **4** can be described as two six-membered rings which are connected by three additional Cu–S bonds, Cu2–S1, Cu4–S5, and Cu5–S4. The atoms Cu1, Cu3, and Cu6 are coordinated in a trigonal planar fashion, each by two sulfur atoms and one phosphorus atom. Cu2 is surrounded by three sulfur atoms, and Cu4 and Cu5 are coordinated tetrahedrally, each by three sulfur atoms and one phosphorus

### Scheme 1. Summary of Reactions

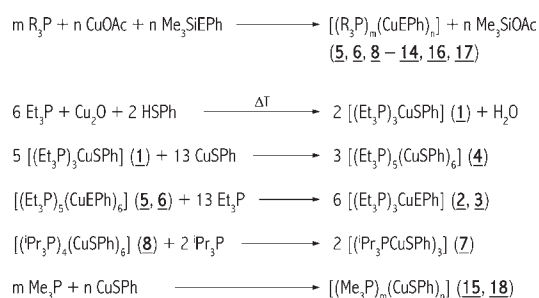


Table 1. Trialkylphosphine-Stabilized Copper(I) Phenylchalcogenolate Complexes **1–18**

E =	S	Se	Te
Me <sub>3</sub> P	$[(Me_3P)_4(CuSPh)_2]$ <b>15</b> $[(Me_3P)_6(CuSPh)_{10}]$ <b>18</b>	$[(Me_3P)_4(CuSePh)_2]$ <b>16</b>	$[(Me_3P)_4(CuTePh)_2]$ <sup>a</sup> <b>17</b>
Et <sub>3</sub> P	$[(Et_3P)_3CuSPh]$ <b>1</b> $[(Et_3P)_5(CuSPh)_6]$ <b>4</b>	$[(Et_3P)_3CuSePh]$ <b>2</b> $[(Et_3P)_5(CuSePh)_6]$ <b>5</b>	$[(Et_3P)_3CuTePh]$ <b>3</b> $[(Et_3P)_5(CuTePh)_6]$ <b>6</b>
<sup>i</sup> Pr <sub>3</sub> P	$[(^iPr_3P)_3CuSPh]$ <b>7</b> $[(^iPr_3P)_4(CuSPh)_6]$ <b>8</b>	$[(^iPr_3P)_4(CuSePh)_6]$ <b>9</b> $[(^iPr_3P)_3(CuSePh)_7]$ <b>10</b>	$[(^iPr_3P)_3(CuTePh)_4]$ <sup>a</sup> <b>11</b>
<sup>t</sup> Bu <sub>3</sub> P	$[(^tBu_3P)_2CuSPh]$ <b>13</b>	$[(^tBu_3P)_2CuSePh]$ <b>14</b>	$[(^tBu_3P)_3(CuTePh)_4]$ <b>12</b>

<sup>a</sup> Lit.<sup>16</sup>

Table 2. Crystallographic Data for Compounds  $[(Et_3P)_m(CuEPh)_n]$ :  $[(Et_3P)_3CuEPh]$  E = S (**1**), Se (**2**), Te (**3**) and  $[(Et_3P)_5(CuEPh)_6]$  E = S (**4**), Se (**5**), Te (**6**)

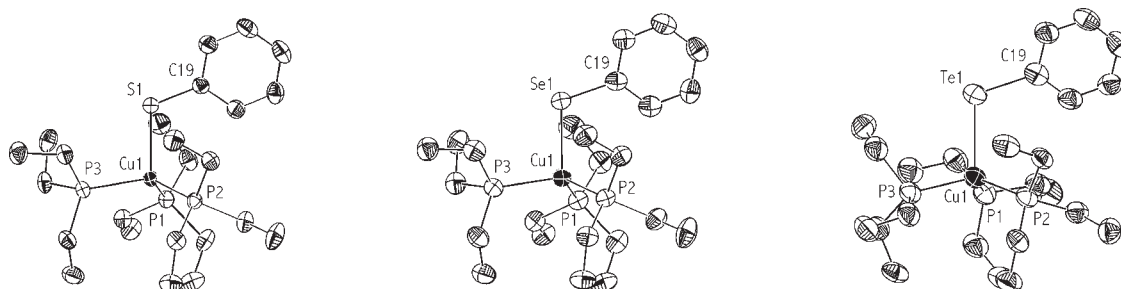
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	5·0.5 C <sub>5</sub> H <sub>12</sub>	<b>6</b>
chemical formula	C <sub>24</sub> H <sub>50</sub> CuP <sub>3</sub> S	C <sub>24</sub> H <sub>50</sub> CuP <sub>3</sub> Se	C <sub>24</sub> H <sub>50</sub> CuP <sub>3</sub> Te	C <sub>66</sub> H <sub>105</sub> Cu <sub>6</sub> P <sub>5</sub> S <sub>6</sub>	C <sub>68.5</sub> H <sub>111</sub> Cu <sub>6</sub> P <sub>5</sub> Se <sub>6</sub>	C <sub>66</sub> H <sub>105</sub> Cu <sub>6</sub> P <sub>5</sub> Te <sub>6</sub>
formula weight [g·mol <sup>-1</sup> ]	527.15	574.05	622.69	1626.95	1938.38	2200.19
space group	Cc (No. 9)	Cc (No. 9)	P2 <sub>1</sub> /n (No. 14)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P2 <sub>1</sub> /n (No. 14)
a [Å]	16.550(1)	16.642(2)	8.9061(9)	13.1180(8)	13.6847(6)	21.6472(6)
b [Å]	10.9479(9)	10.9725(7)	33.255(3)	13.8829(9)	14.9342(6)	15.5979(5)
c [Å]	15.921(1)	16.005(1)	9.998(1)	23.449(1)	22.375(1)	24.1542(7)
α [°]	90	90	90	91.776(5)	92.005(3)	90
β [°]	95.958(5)	95.508(7)	94.643(9)	94.983(5)	103.197(3)	98.176(2)
γ [°]	90	90	90	116.266(4)	114.376(3)	90
V [Å <sup>3</sup> ]	2869.1(3)	2909.1(4)	2951.3(5)	3803.5(4)	4011.8(3)	8072.8(4)
Z	4	4	4	2	2	4
D <sub>calcd</sub> [g·cm <sup>-3</sup> ]	1.220	1.311	1.401	1.421	1.605	1.810
μ [MoK <sub>α</sub> , mm <sup>-1</sup> ]	1.011	2.176	1.881	1.953	4.419	3.811
R <sub>1</sub> [I > 2σ(I)]	0.0275	0.0448	0.0908	0.0407	0.0321	0.0306
wR <sub>2</sub> [all data]	0.0697	0.1199	0.2546	0.1003	0.0729	0.0763

**Table 3.** Crystallographic Data for Compounds  $[(^t\text{Pr}_3\text{P})_m(\text{CuEPh})_n]$ :  $[(^t\text{Pr}_3\text{PCuSPh})_3]$  (7),  $[(^t\text{Pr}_3\text{P})_4(\text{CuEPh})_6]$  E = S (8), Se (9),  $[(^t\text{Pr}_3\text{P})_3(\text{CuSePh})_7]$  (10) and  $[(^t\text{Pr}_3\text{P})_3(\text{CuTePh})_4]$  (11)

	7	8	9	9 · C <sub>5</sub> H <sub>12</sub>	10	11
chemical formula	C <sub>45</sub> H <sub>78</sub> Cu <sub>3</sub> P <sub>3</sub> S <sub>3</sub>	C <sub>72</sub> H <sub>114</sub> Cu <sub>6</sub> P <sub>4</sub> S <sub>6</sub>	C <sub>72</sub> H <sub>114</sub> Cu <sub>6</sub> P <sub>4</sub> Se <sub>6</sub>	C <sub>77</sub> H <sub>114</sub> Cu <sub>6</sub> P <sub>4</sub> Se <sub>6</sub>	C <sub>69</sub> H <sub>98</sub> Cu <sub>7</sub> P <sub>3</sub> Se <sub>7</sub>	C <sub>51</sub> H <sub>83</sub> Cu <sub>4</sub> P <sub>3</sub> Te <sub>4</sub>
formula weight [g · mol <sup>-1</sup> ]	998.78	1677.11	1958.51	2018.56	2017.88	1553.64
space group	<i>P</i> <sub>2</sub> / <i>n</i> (No. 14)	<i>P</i> <sub>2</sub> / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> <sub>2</sub> / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> [Å]	14.0503(7)	14.8375(7)	14.9051(7)	14.9225(7)	16.8095(9)	11.8041(6)
<i>b</i> [Å]	13.4364(4)	15.7165(9)	16.5766(9)	24.362(1)	21.8464(8)	15.1305(9)
<i>c</i> [Å]	26.985(1)	18.4522(8)	18.514(1)	27.153(1)	21.450(1)	18.503(1)
$\alpha$ [°]	90	90	102.399(4)	71.435(3)	90	83.637(5)
$\beta$ [°]	95.093(4)	112.584(3)	103.369(4)	88.298(4)	90.499(4)	80.377(5)
$\gamma$ [°]	90	90	100.992(4)	71.704(4)	90	68.120(4)
<i>V</i> [Å <sup>3</sup> ]	5074.2(4)	3973.0(3)	4205.3(4)	8857.3(7)	7876.9(6)	3019.2(3)
<i>Z</i>	4	2	2	4	4	2
<i>D</i> <sub>calcd</sub> [g · cm <sup>-3</sup> ]	1.307	1.402	1.547	1.514	1.702	1.709
$\mu$ [Mo <i>K</i> $\alpha$ , mm <sup>-1</sup> ]	1.490	1.850	4.199	3.989	5.186	3.393
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0384	0.0377	0.0296	0.0473	0.0312	0.0310
<i>wR</i> <sub>2</sub> [all data]	0.1007	0.0858	0.0703	0.0984	0.0589	0.0786

**Table 4.** Crystallographic Data for Compounds  $[(\text{R}_3\text{P})_m(\text{CuEPh})_n]$  (R = Me, <sup>t</sup>Bu):  $[(^t\text{Bu}_3\text{P})_3(\text{CuTePh})_4]$  (12),  $[(^t\text{Bu}_3\text{PCuEPh})_2]$  E = S (13), Se (14),  $[(\text{Me}_3\text{P})_4(\text{CuEPh})_2]$  E = S (15), Se (16),  $[(\text{Me}_3\text{P})_6(\text{CuSPh})_{10}]$  (18)

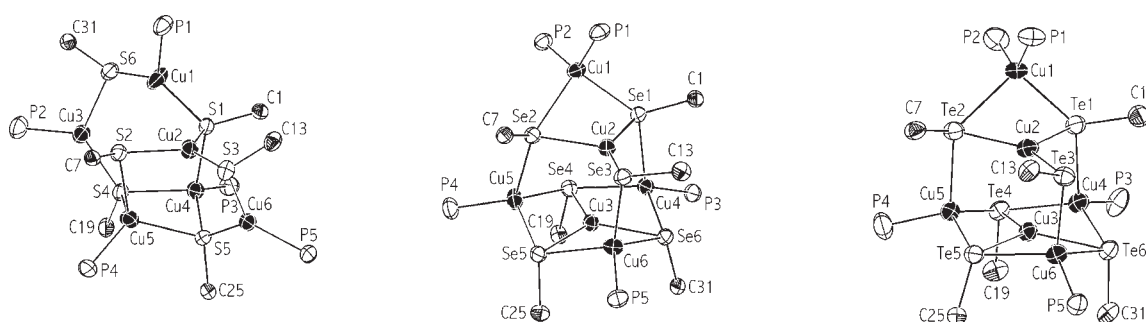
	12	13	14	15	16	18 · CH <sub>3</sub> OH
chemical formula	C <sub>60</sub> H <sub>101</sub> Cu <sub>4</sub> P <sub>3</sub> Te <sub>4</sub>	C <sub>36</sub> H <sub>64</sub> Cu <sub>2</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>36</sub> H <sub>64</sub> Cu <sub>2</sub> P <sub>2</sub> Se <sub>2</sub>	C <sub>24</sub> H <sub>46</sub> Cu <sub>2</sub> P <sub>4</sub> S <sub>2</sub>	C <sub>24</sub> H <sub>46</sub> Cu <sub>2</sub> P <sub>4</sub> Se <sub>2</sub>	C <sub>79</sub> H <sub>107</sub> Cu <sub>10</sub> OP <sub>6</sub> S <sub>10</sub>
formula weight [g · mol <sup>-1</sup> ]	1679.88	750.01	843.81	649.69	743.49	2214.47
space group	<i>Pccn</i> (No. 56)	<i>P</i> <sub>2</sub> / <i>c</i> (No. 14)	<i>P</i> <sub>2</sub> ,2 <sub>1</sub> (No. 19)	<i>P</i> <sub>2</sub> / <i>n</i> (No. 14)	<i>P</i> <sub>2</sub> / <i>c</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)
<i>a</i> [Å]	18.1425(4)	13.0681(7)	10.8035(5)	10.8449(6)	17.0556(9)	28.423(1)
<i>b</i> [Å]	23.7058(6)	25.049(1)	16.1997(8)	10.9060(6)	13.6841(8)	13.5129(5)
<i>c</i> [Å]	31.4413(6)	13.1012(8)	22.5376(8)	14.3336(9)	14.0034(7)	25.2897(9)
$\alpha$ [°]	90	90	90	90	90	90
$\beta$ [°]	90	113.356(4)	90	102.679(5)	91.081(4)	105.633(3)
$\gamma$ [°]	90	90	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	13522.4(5)	3937.2(4)	3944.4(3)	1654.0(2)	3267.7(3)	9353.7(6)
<i>Z</i>	8	4	4	2	4	4
<i>D</i> <sub>calcd</sub> [g · cm <sup>-3</sup> ]	1.650	1.265	1.421	1.305	1.511	1.570
$\mu$ [Mo <i>K</i> $\alpha$ , mm <sup>-1</sup> ]	3.038	1.290	3.027	1.617	3.737	2.591
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0323	0.0264	0.0358	0.0255	0.0250	0.0271
<i>wR</i> <sub>2</sub> [all data]	0.0857	0.0714	0.0672	0.0684	0.0504	0.0629

**Figure 1.** Molecular structures of compounds  $[(\text{Et}_3\text{P})_3\text{CuEPh}]$ , E = S (1), Se (2), Te (3). Hydrogen atoms omitted, 50% probability ellipsoids.

atom. Additionally, a secondary Cu–S connection between Cu1 and S2 is observed, their distance is 290.38(9) pm, and Cu1 is 31 pm out of the plane defined by P1, S1, and S6.

A different structure is found for compounds 5 and 6. In these complexes the six chalcogen atoms form a distorted octahedron

with three faces capped by the atoms Cu4, Cu5, and Cu6. The tetrahedral coordination sphere of these copper atoms is completed by one phosphine ligand each. Cu1 is coordinated by two phosphine ligands and bridges the edge E1–E2 of the octahedron. The atoms Cu2 and Cu3 each lie on the center of opposite



**Figure 2.** Molecular structures of compounds  $[(\text{Et}_3\text{P})_5(\text{CuEPh})_6]$ ,  $\text{E} = \text{S}$  (4),  $\text{Se}$  (5),  $\text{Te}$  (6). Thermal ellipsoids are drawn at 50% probability level. Hydrogen and carbon atoms are omitted; only carbon atoms bound to chalcogen atoms are shown.



**Figure 3.** Molecular structures of  $[(^1\text{Pr}_3\text{PCuSPh})_3]$  (7) and  $[(^1\text{Pr}_3\text{P})_4(\text{CuSPh})_6]$  (8). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and  $^1\text{Pr}$ -groups are omitted.

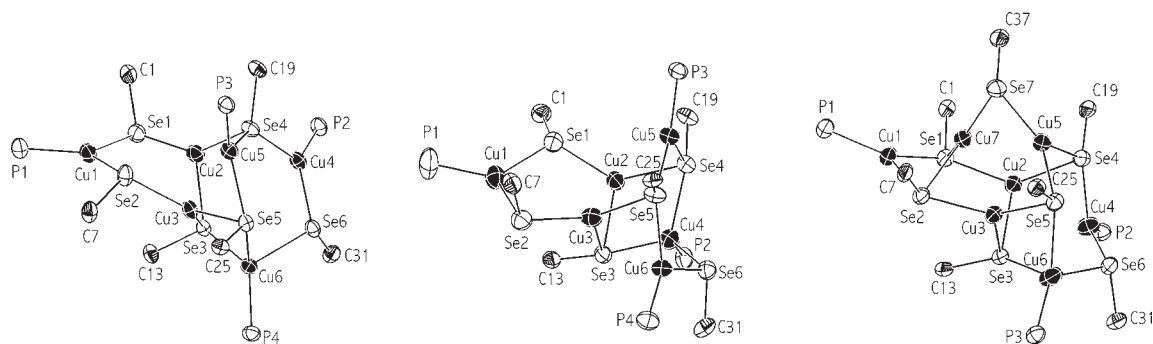
faces of the octahedron and therefore are trigonal planar. Note that the trigonal planar coordination of Cu2 by E1, E2, and E3 is the only structural similarity between 4 and 5 and 6. The cage structure found for 5 and 6 is identical with that of the compounds  $[(\text{Ph}_2\text{EtP})_5(\text{CuTePh})_6]$ <sup>14</sup> and  $[(\text{Ph}_3\text{P})_5(\text{AgSC}_6\text{H}_4\text{Cl})_6]$ .<sup>15</sup> Interestingly, Corrigan and co-workers obtained the related ionic compound  $[\text{Et}_3\text{PPh}]^+[(\text{Et}_3\text{P})_3\text{Cu}_5(\text{TePh})_6]^-$ .<sup>16</sup> The anionic part of this structure is identical with 6, if the  $(\text{Et}_3\text{P})_2\text{Cu}^+$ -moiety bridging Te1 and Te2 in 6 is removed.

With triisopropylphosphine as a ligand we obtained two phenylthiolate complexes  $[(^1\text{Pr}_3\text{PCuSPh})_3]$  (7) and  $[(^1\text{Pr}_3\text{P})_4(\text{CuSPh})_6]$  (8). These two structures are shown in Figure 3. The trinuclear complex 7 consists of a nearly planar  $\text{Cu}_3\text{S}_3$  ring with a phosphine ligand coordinated to each copper atom. Not only the copper atoms but also the sulfur atom S2 display a trigonal planar environment, a rare case which will be addressed more extensively in a later section.

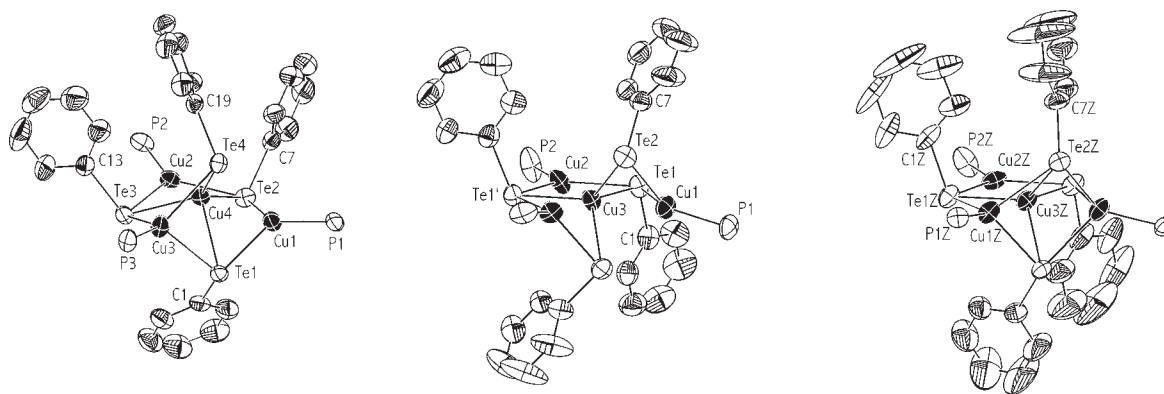
The asymmetric unit of the hexanuclear complex 8 is again a  $\text{Cu}_3\text{S}_3$ -ring. By the crystallographic inversion center the complete molecule is created, which therefore has the point group symmetry  $C_i$ . The two six-membered rings are connected by four additional Cu–S bonds (Cu2–S1', Cu3–S2', Cu2'–S1, and Cu3'–S2). Atom Cu2 and its symmetry equivalent are tetrahedrally coordinated by three sulfur atoms and one phosphorus atom. The bond Cu2–S1' with 267.06(9) pm is extraordinarily long, so one can state that this copper atom is intermediate between tetrahedral and trigonal planar coordination. The other copper atoms are trigonal planar, Cu1 is coordinated by one phosphine ligand and two sulfur atoms, and Cu3 by three sulfur atoms. Overall, the copper atoms as well as the sulfur atoms form an octahedron each, both octahedra interpenetrating each other.

Compound 8 can be easily converted to compound 7 by adding the necessary 2 equiv of triisopropylphosphine per mole of 8.

Accessible selenium compounds with triisopropylphosphine ligands are  $[(^1\text{Pr}_3\text{P})_4(\text{CuSePh})_6]$  (9) and  $[(^1\text{Pr}_3\text{P})_3(\text{CuSePh})_7]$  (10). Their structures are shown in Figure 4. The structure of compound 9 can be described as a tetrahedron of selenium atoms (Se3, Se4, Se5, and Se6). One tetrahedral face is capped by Cu6, and four edges are bridged by Cu2, Cu3, Cu4, and Cu5, respectively. The atoms Cu2 and Cu3 bind to Se1 and Se2, which form further bonds to Cu1, giving a six-membered ring together with Se3. The copper atoms are trigonal planar, except Cu6 which is tetrahedrally coordinated but has a very long bond of 270.15(5) pm to Se5 and is therefore intermediate between tetrahedral and trigonal planar coordination. The atom Cu5 is 32 pm out of the plane defined by P3, Se4, and Se5, indicating a weak secondary Cu–Se connection, since the distance between Cu5 and Se2 is 363.69(5) pm. Compound 9 can also be crystallized with pentane. The triclinic unit cell volume is doubled then, and the asymmetric unit consists of two independent molecules, which differ in their organic periphery; for example, the conformations of the phosphine ligands P3 and P4 are not identical. The heavy atoms of the second molecule form nearly the same framework as found in the solvent-free structure, but the long bond Cu6–Se5 appears to be somewhat shorter here (262.5(1) pm). The secondary connection between Cu5 and Se2 is weaker with a distance of 367.3(1) pm and an out-of-plane parameter of 26 pm for Cu5. In the first molecule a Cu5–Se2 distance of 413.0(1) pm and an out-of-plane parameter of only 13 pm is observed. The bond between Cu6 and Se3 is replaced by a secondary connection in the first molecule, the distance is 325.8(1) pm and Cu6 is 20 pm out of the plane defined by



**Figure 4.** Molecular structures of  $[(^i\text{Pr}_3\text{P})_4(\text{CuSePh})_6]$  (**9**) (left: solvent-free; middle: first molecule from **9**·pentane) and  $[(^i\text{Pr}_3\text{P})_3(\text{CuSePh})_7]$  (**10**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen and carbon atoms are omitted; only carbon atoms bound to chalcogen atoms are shown.



**Figure 5.** Molecular structures of  $[(\text{R}_3\text{P})_3(\text{CuTePh})_4]$ ,  $\text{R} = ^i\text{Pr}$  (**11**, triclinic phase) and  $^t\text{Bu}$  (**12**, two independent molecules). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and carbon atoms of alkyl groups are omitted.

Se5, Se6, and P4. Instead, Cu4 is the tetrahedrally coordinated atom then. Therefore, Se3 shows the tendency to bridge four copper atoms.

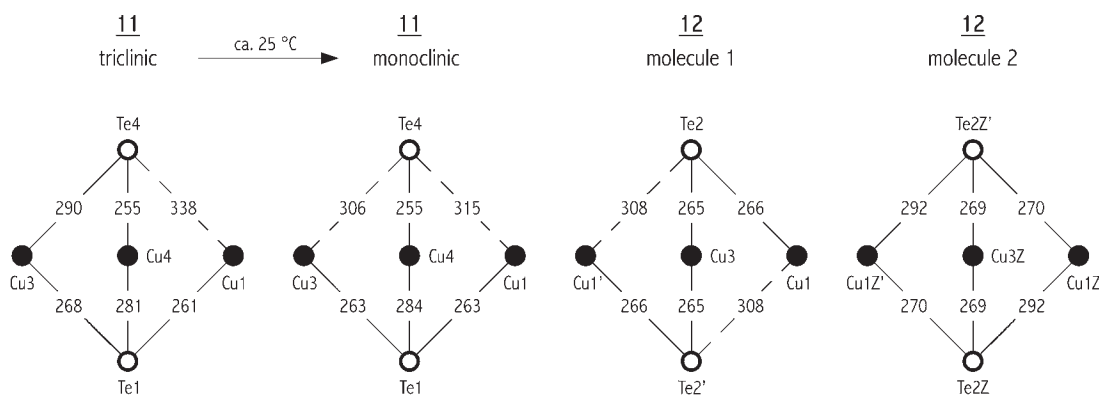
The structure of **10** is related to that of **9** by replacing the phosphine ligand at Cu5 with an CuSePh moiety, which forms additional bonds to Se1 and Se2. The result is an octahedron of selenium atoms (Se1 to Se5 and Se7) and a tetrahedron of trigonal planar copper atoms (Cu2, Cu3, Cu5, and Cu7). This central core resembles the ion  $[\text{Cu}_4(\text{SePh})_6]^{2-}$ .<sup>9</sup> The Se1–Se2 edge of the octahedron is bridged by Cu1 and the Se3–Se5 edge by Cu6. The bond length of Cu6–Se3 is 281.69(6) pm, which is a borderline case between a bond and a secondary connection, so Cu6 is intermediate between tetrahedral and trigonal planar coordination. A secondary Cu–Se connection is observed between Cu4 and Se3, their distance is 324.63(6) pm and Cu4 is 35 pm out of the plane defined by P2, Se4, and Se6, so Cu4 is on the way to tetrahedral coordination, too. This leads to approximate  $C_s$ -symmetry for the heavy atom framework, and Se3 shows the tendency to bridge four copper atoms.

The monoclinic phase of  $[(^i\text{Pr}_3\text{P})_3(\text{CuTePh})_4]$  (**11**) has been reported before.<sup>16</sup> If synthesis and crystallization are performed at low temperatures, a metastable triclinic phase is obtained, which converts to the reported monoclinic phase at room temperature. The compound  $[(^t\text{Bu}_3\text{P})_3(\text{CuTePh})_4]$  (**12**) exhibits a very similar structure. The two structures are shown in Figure 5.

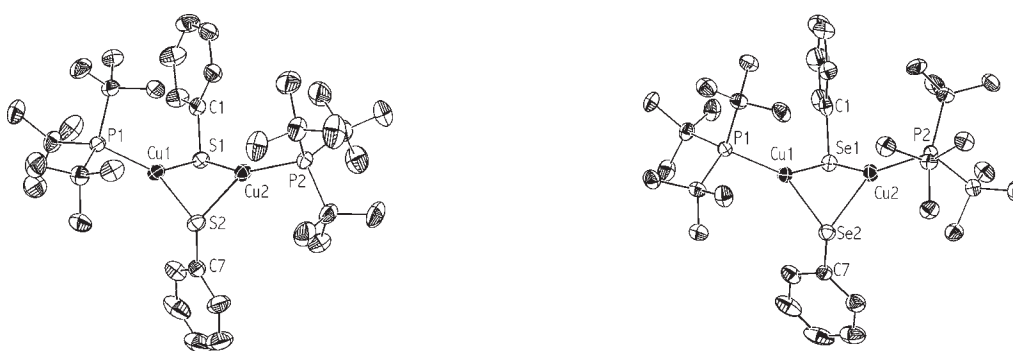
These tetranuclear complexes consist of a centered  $[(\text{R}_3\text{P})_3\text{Cu}_4(\text{TePh})_3]^+$  ring system, which is also part of compound **6**. An additional  $\text{TePh}^-$  ligand completes these molecules. The

asymmetric unit of compound **12** consists of two independent half molecules, each containing a 2-fold rotation axis. A significant difference going from  $^i\text{Pr}_3\text{P}$  to  $^t\text{Bu}_3\text{P}$  is the orientation of the phenyl groups attached to Te2 and Te3 in **11** and Te1 and Te1' in **12**. The former are in *syn*-position, the latter in *anti*-position. Further differences are slightly elongated Cu2–Te bonds in **12** due to the larger phosphine ligand. The most striking differences are found in the opposite side of the ring system, relative to Cu2. A schematic representation of the Cu–Te connectivities in this part of the molecules is given in Figure 6.

The short bond between Cu4 and Te4 in **11** remains unchanged when the phase transition occurs, while the very long bond between Cu4 and Te1 is further elongated. The respective bonds in **12** are equal by symmetry, and therefore the coordination of the central atom Cu4 is more tetrahedral in **12**. In **11** the atom Cu4 is only 22 pm (triclinic phase) or 19 pm (monoclinic phase) out of the plane defined by Te2, Te3, and Te4, so the coordination sphere is trigonal pyramidal rather than tetrahedral. The coordination spheres of the atoms Cu1 and Cu3 in **11** are intermediate between trigonal planar and tetrahedral, since all the distances to Te4 are large. In the triclinic phase Cu3 is more tetrahedrally coordinated, with a very long bond of 289.83(6) pm to Te4, while Cu1 is better described as trigonal planar with a secondary connection (337.88(6) pm) to Te4, resulting in an out-of-plane parameter of 31 pm for Cu1 based on P1, Te1, and Te2. After phase transition to the monoclinic crystal system, the connections between Te4 and copper atoms Cu1 and Cu3 both



**Figure 6.** Schematic representation of different Cu–Te distances [pm] in  $[(R_3P)_3(CuTePh)_4]$ ,  $R = iPr$  (**11**) and  $tBu$  (**12**).



**Figure 7.** Molecular structures of compounds  $[(tBu_3PCuEPh)_2]$ ,  $E = S$  (**13**) and  $Se$  (**14**). Hydrogen atoms omitted, 50% probability ellipsoids.

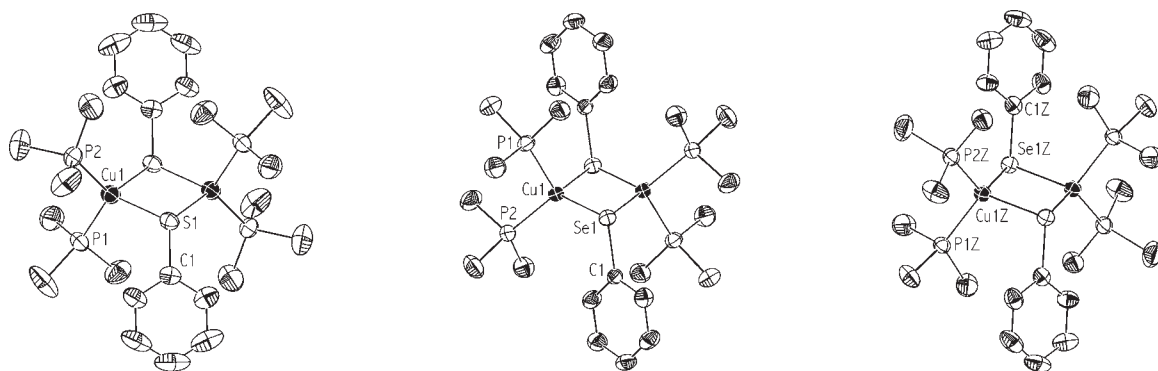
are secondary. It was stated that the phenyltelluroate ligand  $Te_4$  is perhaps best described as “pseudo-terminal”,<sup>16</sup> a statement we agree with, since the bond  $Cu_4-Te_4$  is even 13 pm shorter than the  $Cu-Te$  bond in compound **3**, where the phenyltelluroate ligand is terminal. In the first molecule of **12**, one bond is of usual length ( $Cu_1-Te_2$ ) and a secondary connection of 308.26(6) pm is observed between  $Cu_1$  (47 pm out of plane) and  $Te_2'$ . In the second molecule, the respective atoms are all connected by bonds, with the overall longest  $Cu-Te$  bond distance of 291.6(1) pm between  $Cu_1$  and  $Te_2$ . In fact, this bond shows some properties of a secondary  $Cu-Te$  connection and may therefore be described as a borderline case.

With  $tBu_3P$  and the lighter chalcogens, we obtained the dinuclear complexes  $[(tBu_3PCuEPh)_2]$  with  $E = S$  (**13**) and  $E = Se$  (**14**). The structures are shown in Figure 7. The copper atoms are trigonal planar with two bonds to the chalcogen atoms and one to phosphorus. Because of the bulky phosphine ligands these systems are sterically crowded, resulting in one  $EPh^-$  moiety coordinating with elongated bond lengths. The maximum difference between  $Cu-E$  bond lengths is 16 pm in **13** and 13 pm in **14**, showing some relaxation due to the larger  $Cu_2E_2$ -core in **14**. The angle  $P_2-Cu_2-S_1$  in **13** is  $146.35(2)^\circ$ , which is nearly half way to linear coordination. The phenyl groups are in anti-position and the four-membered rings are folded along the vector  $Cu_1-Cu_2$  ( $44^\circ$  in **13** and  $52^\circ$  in **14**).

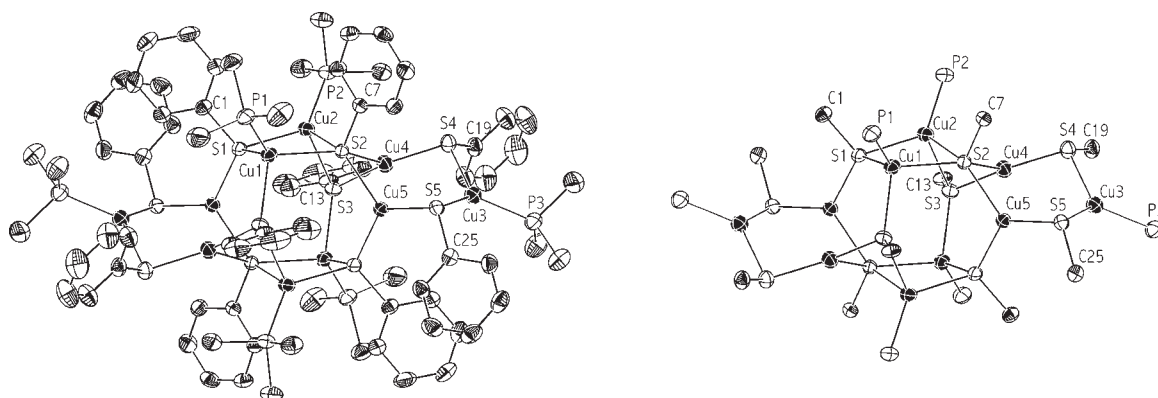
Other dinuclear complexes can be obtained with 2 equiv of trimethylphosphine. The structures of  $[(Me_3P)_4(CuEPh)_2]$  with  $E = S$  (**15**) and  $E = Se$  (**16**) are shown in Figure 8. The homologous tellurium compound (**17**) has been described already<sup>16</sup> and is isomorphous with **16**. The asymmetric unit of

**15** consists of half a molecule. The complete molecules are centrosymmetric. For **16** there are two independent half molecules in the asymmetric unit, generating two different molecules with inversion symmetry. Therefore, the four-membered rings are exactly planar and the phenyl groups are in anti-position. The copper atoms are coordinated tetrahedrally by two phosphine ligands and two bridging phenylchalcogenolates. In **15** the two independent  $Cu-S$  bonds have the same length (238.83(5) pm and 238.93(4) pm) and the planes of the phenyl groups are approximately perpendicular to the plane defined by the two sulfur atoms and  $C_1$ , so the molecule has approximately  $C_{2h}$ -symmetry. In **16** a short and a long  $Cu-Se$  bond can be distinguished for each molecule, and the difference is about 5 pm. Interestingly, the shorter bond is found with the phenyl ring in plane, which is contrary to what one would expect from sterical considerations. As was found for **17**,<sup>16</sup> the two independent molecules differ in their  $Cu-E-Cu$  angles. The difference for **17** was reported to be about  $8^\circ$ , and in **16** it is  $6^\circ$ . A  $^{77}Se$ -NMR signal at  $-39$  ppm could be observed for compound **16**. Note that the homologous oxygen compound  $[(Me_3P)_4(CuOPh)_2]$  was also characterized structurally.<sup>19</sup> In contrast to **15**, **16**, and **17** the phenyl rings are in plane with the  $Cu_2O_2$  ring.

A further phenylthiolate compound coordinated by trimethylphosphine could be isolated. The structure of the decanuclear complex  $[(Me_3P)_6(CuSPh)_{10}]$  (**18**) is shown in Figure 9. The asymmetric unit contains half a molecule, and the complete molecules have the point group symmetry  $C_i$ . The inner core containing the atoms  $Cu_1, Cu_2, Cu_5, S_1, S_2, S_3$  and their symmetry equivalents resemble the structure of the hexanuclear complex **8**, with two interpenetrating octahedra of sulfur and



**Figure 8.** Molecular structures of compounds  $[(\text{Me}_3\text{P})_4(\text{CuEPh})_2]$ ,  $\text{E} = \text{S}$  (**15**) and  $\text{Se}$  (**16**, two independent molecules). Hydrogen atoms are omitted, 50% probability ellipsoids.



**Figure 9.** Molecular structure of  $[(\text{Me}_3\text{P})_6(\text{CuSPh})_{10}]$  (**18**). Thermal ellipsoids are drawn at the 50% probability level. Left: hydrogen atoms omitted; right: only the heavy atom framework with carbon atoms bound to sulfur atoms is shown.

**Table 5. Minimal, Average, and Maximal Cu–E Bond Lengths [pm] Found in Compounds 1–18**

E	minimal	average	maximal
	Cu(3-fold coordinated)-E [pm]		
S	219	227	246
Se	232	241	257
Te	251	261	267
	Cu(4-fold coordinated)-E [pm]		
S	232	240	267
Se	243	254	282
Te	255	268	292

copper atoms, respectively. In **18** the atoms Cu4 and S5 bind to the  $\text{Cu}_6\text{S}_6$ -core and are connected by Cu3 and S4, giving a six-membered ring together with Cu5 and S2. Atoms Cu1 and Cu2 are coordinated tetrahedrally by one phosphorus and three sulfur atoms, and the other three copper atoms are trigonal planar. Atom S2 bridges four copper atoms, which is a rare case. As a result, the Cu–S bonds in this structure span a wide range from 219.29(7) pm for Cu4–S4 to 245.79(6) pm for Cu4–S2. The coordination of Cu4 can be stated to be intermediate between trigonal planar and linear, as the bond angle S3–Cu4–S4 is 155.61(3)°.

**2. Comparison of Structural Data.** Table 5 gives minimal, average, and maximal Cu–E bond lengths found in compounds

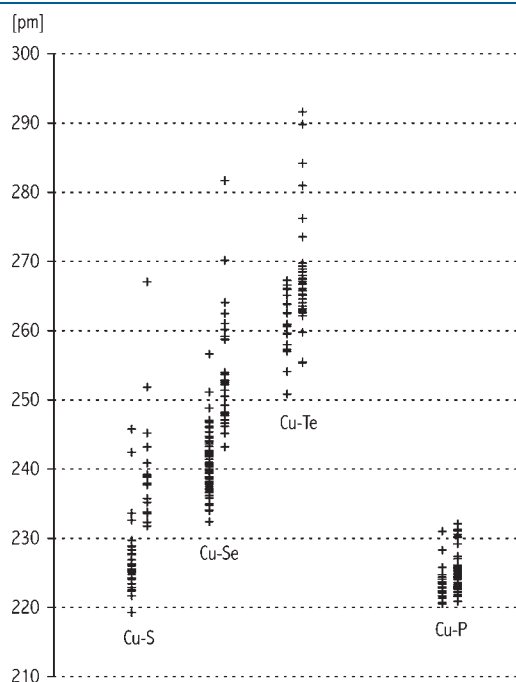
**Table 6. Distances for Secondary Cu–E Connections in Compounds 1–18, Out-of-Plane Parameters (o. o. p.) for the Respective Copper Atom and Cu–E–C Angles**

E	compound	Cu–E [pm]	oopp [pm]	Cu–E–C [deg]
S	<b>4</b>	290.38(9)	31.15(6)	129.2(1)
Se	<b>10</b>	324.63(6)	34.80(4)	140.8(1)
	<b>9</b> ·pentane	325.8(1)	20.13(9)	152.9(2)
	<b>9</b>	363.69(5)	32.32(4)	122.05(9)
	<b>9</b> ·pentane	367.3(1)	25.75(8)	122.7(2)
Te	<b>11</b>	305.58(7)	45.38(6)	120.4(1)
	<b>12</b>	308.28(6)	47.17(5)	137.3(1)
	<b>11</b>	314.83(7)	49.15(5)	132.3(1)
	<b>11</b>	337.88(6)	30.80(5)	134.1(1)

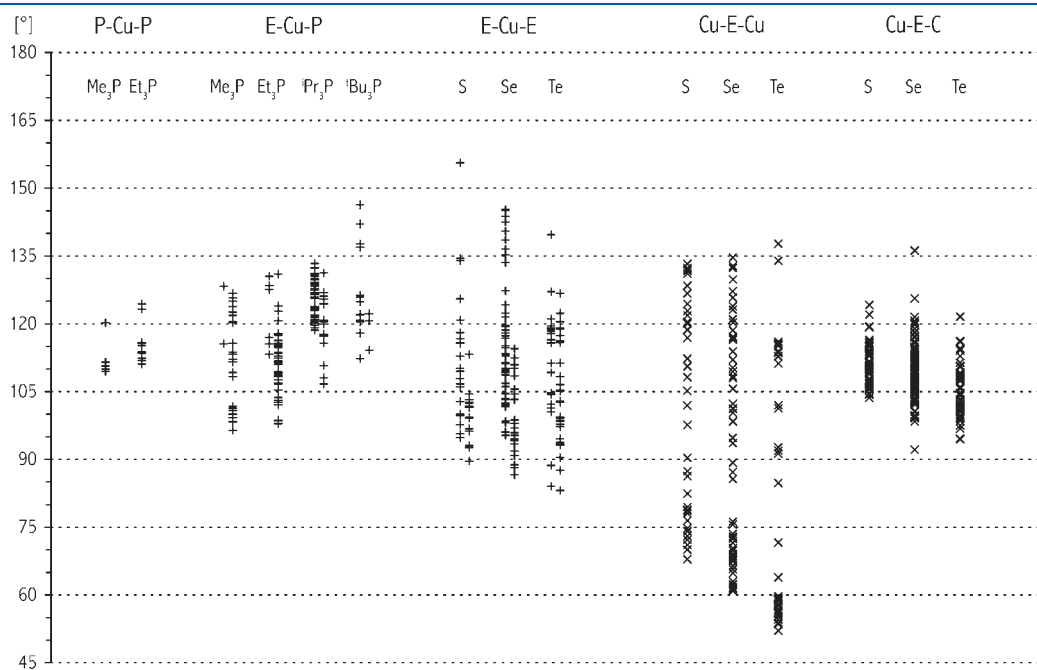
**1–18.** For 4-fold coordinated copper the maximal bond lengths represent cutoff values chosen to separate bonds and secondary connections (compare Table 6). Especially in the case of tellurium compounds this separation is somewhat arbitrary. Counting all secondary connections as bonds would result in unreasonably long bonds and distorted mean values.

There is a clear dependency of the Cu–E bond length on the coordination mode of the copper atom. For  $\text{E} = \text{S}$  this dependency causes nearly a separation into two groups, as Cu–S bond lengths for 3-fold coordinated copper rarely exceed 230 pm, while 4-fold coordinated copper has exclusively Cu–S bonds

longer than 230 pm. This is also illustrated in Figure 10. This separation is somewhat less clear for E = Se and Te, the latter showing a much smaller difference of the average values (13 pm for S and Se, 7 pm for Te). Intermediate cases in coordination mode result in one extremely large bond length. All the long bonds for tetrahedral coordination correspond to a beginning transition toward trigonal planar coordination. The two longest Cu–S bonds for 3-fold coordinated copper are related



**Figure 10.** Plot of Cu–E and Cu–P bond lengths in compounds 1–18. Values for 3-fold coordinated copper are shown in the left and for 4-fold coordinated copper in the right columns, respectively.



**Figure 11.** Plot of bond angles at copper and chalcogen atoms in compounds 1–18. In the case of E–Cu–P and E–Cu–E angles values for 3-fold coordinated copper are shown in the left and for 4-fold coordinated copper in the right columns, respectively.

to intermediate cases between trigonal planar and linear coordination.

For 3-fold coordinated copper, we observed secondary Cu–E connections with even longer distances. They represent a beginning transition from trigonal planar to tetrahedral coordination and usually express in enlarged out-of-plane parameters (20–50 pm) and strongly deformed thermal ellipsoids at the affected copper atom, giving rise to large Hirshfeld differences.<sup>20</sup>

The Cu–P bonds are less flexible, as can be seen in Figure 10. Average values are 223 and 226 pm for 3-fold and 4-fold coordinated copper, respectively. No dependence on the size of the alkyl groups could be found, and it seems that steric and electronic effects (increased donor capability for larger alkyl groups) cancel out. The longest Cu–P bonds are found in the phosphine-rich mononuclear complexes 1–3. The E–C bonds are rigid. Average values are 177, 193, and 213 pm for E = S, Se, and Te, respectively. The largest deviations from these values are found for the overall shortest E–C bonds in complexes 1–3 (174.6(3) pm, 190.4(6) pm, and 211(1) pm).

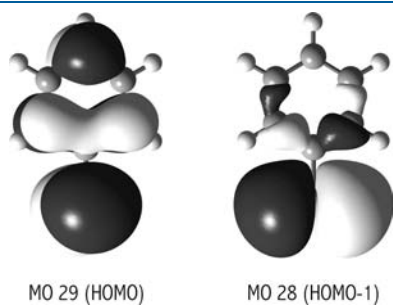
The coordination spheres of the copper atoms are generally distorted. As illustrated in Figure 11, angles E–Cu–P and E–Cu–E span a wide range for both 3-fold and 4-fold coordinated copper. Ideal values of 120° and 109° are matched only occasionally. At least for the smaller phosphine ligands, the average angles E–Cu–P are close to ideal values with 122° and 111° for both Me<sub>3</sub>P and Et<sub>3</sub>P. For the larger phosphines, these average values exceed the ideal values with 126° and 120° for <sup>i</sup>Pr<sub>3</sub>P and 127° and 119° for <sup>t</sup>Bu<sub>3</sub>P. Angles E–Cu–E tend to be smaller than ideal, as the average values for 3-fold coordinated copper are 113°, 116°, and 111° for E = S, Se, and Te. For 4-fold coordinated copper, these values are 100° for S and Se and 105° for Te. Note that the average values for tellurium are much closer to each other than for sulfur and selenium.

Extremely large variations are observed for Cu–E–Cu angles, which show values between 50° and 140° (Figure 11). The increasing range going from sulfur to tellurium can be attributed

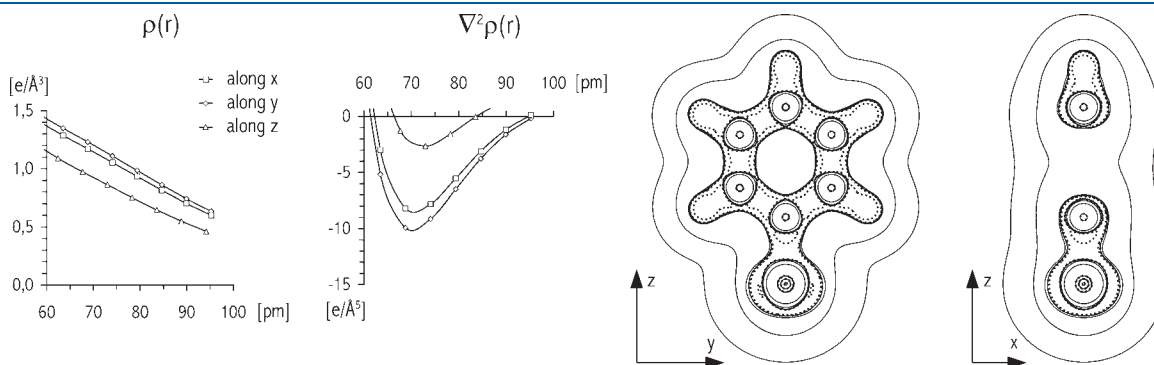


to the higher polarizability for the heavier chalcogens. Cu–E–C angles are more rigid (Figure 11). Their mean values are 111°, 109°, and 105° for S, Se, and Te, respectively. Cu–E–C angles do not only span a relatively sharp range but are approximately normal distributed around their mean values, emphasizing their rigidity. Usually, deviations are found to be less than 15°, and outliers are related to borderline cases between Cu–E bonds and secondary Cu–E connections. The two largest values for E = Se are 126° and 136°. Both are found in compound **10** and correspond to the long Cu6–Se bonds (264.08(7) pm and 281.69(6) pm, respectively). The largest value for E = Te is 122° and corresponds to the long bond between Cu1 and Te2 in the second molecule of compound **12** (291.6(1) pm). Note that the respective Cu–Te distance is 308.28(6) pm in the first molecule and results in a Cu–Te–C angle of 137.3(1)°. In Table 6, the secondary Cu–E connections are listed together with the respective Cu–E–C angles. Obviously, the rigidity gets lost when the respective Cu–E distance is elongated. So it may be concluded that the Cu–E–C angles can help to distinguish between long Cu–E bonds and secondary Cu–E connections.

**3. DFT Calculations.** We performed DFT(B3LYP) calculations on simple model systems to get a deeper insight in the electronic structure, which may be helpful to explain the observed phenomena. At first, it is useful to take a look into the system SPh<sup>−</sup>. In terms of molecular orbital theory, the two highest occupied molecular orbitals (Figure 12) are located mainly at the sulfur atom and are of *p*-character, pointing perpendicular to the S–C bond. Regarding these orbitals as sulfur lone-pairs, there is a charge delocalization toward the phenyl  $\pi$ -system in the highest occupied molecular orbital (HOMO).



**Figure 12.** The two highest occupied orbitals in the system SPh<sup>−</sup> as derived from DFT(B3LYP) calculations. The surface represents the isovalue of 0.02.



**Figure 13.** Plots of charge density  $\rho(r)$  and its second derivative (Laplacian) in the system SPh<sup>−</sup> as derived from DFT(B3LYP) calculations. The *z*-axis coincides with the S–C bond. Left: one-dimensional plots dependent on the distance from the sulfur atom. Right: two-dimensional plots of the Laplacian in a plane with the phenyl ring and perpendicular to this plane.

In terms of charge density analysis, the charge distribution around the chalcogen atom is rather asymmetrical. As shown in Figure 13, the charge density  $\rho(r)$  is distinctly higher in directions perpendicular to the S–C bond. This can be seen even more clearly in the second derivative (Laplacian) of the charge density, which can be interpreted as charge concentration where negative.<sup>21</sup>

Introducing a Cu<sup>+</sup> ion in this system, one can expect a (covalent) Cu–S  $\sigma$ -bond to be formed along the directions of the two highest occupied MOs to obtain an effective overlap.<sup>22</sup> As a result, the Cu–S–C bond angle can be expected to be highly bent. Calculations for the systems CuEPH (E = S, Se) give a minimum on the potential energy surface for a bent Cu–E–C arrangement (point group symmetry  $C_s$ ) with bond angles of 103° and 100° for S and Se, respectively, while the linear Cu–E–C arrangement (point group symmetry  $C_{2v}$ ) is found to be a second-order saddle point, 126 and 144 kJ/mol above the minimum for S and Se, respectively. Similar results were obtained for systems CuESiH<sub>3</sub> (E = O, S, Se), and a detailed bond and charge density analysis revealed that bending of the Cu–E–Si angle reduces Pauli repulsion and leads to an increased covalent interaction between the copper and the chalcogen atom.<sup>23</sup> It has been shown further that the bending potential of the Cu–O–Si angle is much flatter than for the heavier chalcogens, since the Cu–O bond is more ionic anyhow. Other related examples are the terminally bonded phenylchalcogenolates in Cp<sup>\*</sup><sub>2</sub>Zr(EPH)<sub>2</sub> (E = O, S, Se, Te), which show the same trend.<sup>24</sup> For the structures presented here, it may be concluded that the secondary Cu–E connections are more electrostatic (ionic) in nature, since the respective Cu–E–R angles are not bent in the usual way, which would be a precondition for effective orbital overlap and therefore for a covalent bond.

Regarding bridging phenylchalcogenolate ligands, one can expect that all Cu–E–C bond angles will be bent in a similar manner, but it may be more convenient to consider the inclination angle  $\phi$  of the E–C vector toward the respective Cu–E–Cu plane (Figure 14).

For a simple  $C_s$ -symmetrical system Cu<sub>2</sub>EPH<sup>+</sup> we define  $\tau$  as the angle Cu–E–C and  $v$  as half the angle Cu–E–Cu. As can be derived from the definition of the cosine in a rectangular triangle and the scalar product of vectors E–Cu and E–C, these three angles are related by their cosines as given in eq 1:

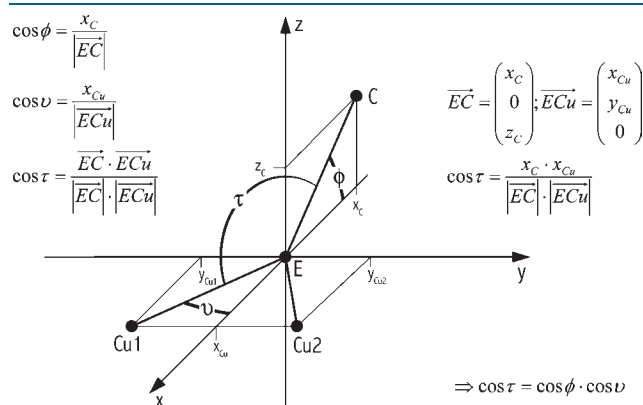
$$\cos \phi = \cos \tau / \cos v \quad (1)$$

For a given (rigid) Cu–E–C angle  $\tau$ , the inclination angle  $\phi$  is then simply a function of  $v$ . Therefore, one can expect a

correlation between  $\phi$  and the Cu–E–Cu angle  $2\nu$ . And in fact, despite their flexibility, Cu–E–Cu angles  $2\nu$  are correlated to inclination angles  $\phi$  (Figure 15). In 1–18, the worst correlation is obtained for two data pairs involving the borderline case bond Cu6–Se3 of 281.69(6) pm in compound 10.

Note that this correlation has been observed by Dance and co-workers for  $\mu_2$ -bridging SPh-groups in the system  $[(\text{Ph}_3\text{P})_4(\text{CuSPh})_3]$ .<sup>12</sup> Examination of related systems, like the planar  $\text{Fe}_3(\text{SPh})_3$  core<sup>25</sup> in  $[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]^{3-}$ , indicated that this correlation may be of general interest for transition metal thiolates and therefore also for metallo–cystein proteins. To our knowledge, this relationship was not extended to higher bridging modes or heavier chalcogens, nor was an explanation given.

Not surprising, this phenomena can be reproduced on DFT-(B3LYP) level of theory. For the simple model system  $\text{Cu}_2\text{EPh}^+$

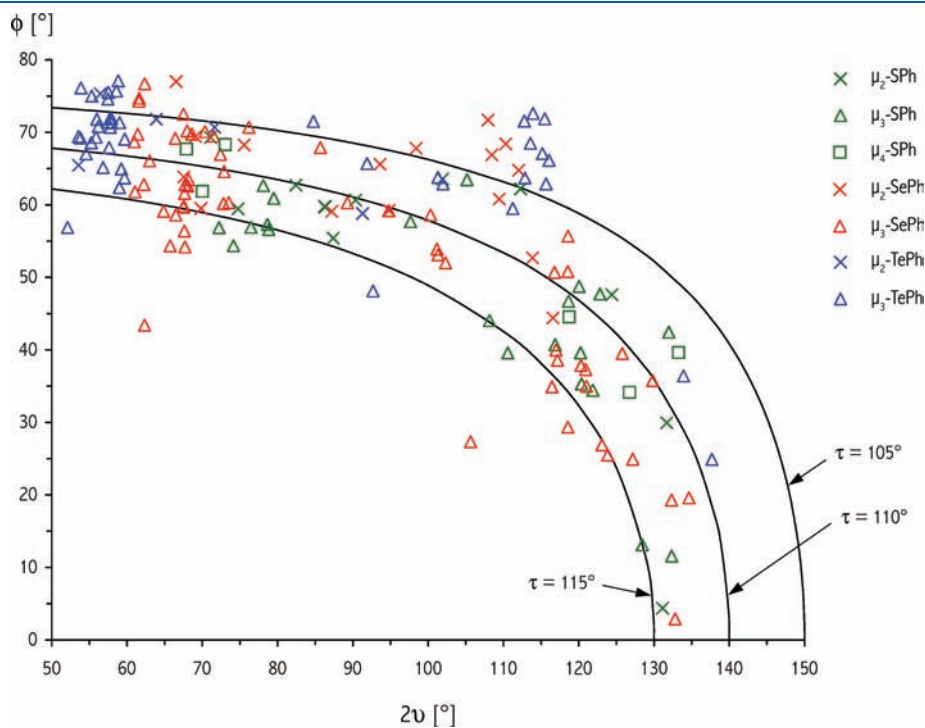


**Figure 14.** Bridging chalcogenolate ligand, definition of angles  $\phi$ ,  $\tau$ , and  $\nu$  in this system, and a short derivation of eq 1.

one obtains two different minima in  $C_s$ -symmetry, according to the rotational angle of the phenyl ring. Chalcogen atoms are pyramidal and data pairs  $2\nu$ ,  $\phi$  are  $76.1^\circ$ ,  $69.9^\circ$  and  $101.7^\circ$ ,  $65.7^\circ$  for E = S and  $71.1^\circ$ ,  $74.2^\circ$  and  $96.9^\circ$ ,  $71.1^\circ$  for E = Se. The respective minima differ less than 3 kJ/mol in energy and the respective transition state was found to be less than 5 kJ/mol above the lowest minimum, so phenyl rings can rotate nearly free in this system. Optimizations for planar chalcogen atoms ( $\phi = 0^\circ$ , point group symmetry  $C_{2v}$ ) gave transition states with  $2\nu = 134.3^\circ$  and  $135.3^\circ$  for E = S and Se. The phenyl ring is perpendicular to the Cu–E–Cu plane in this case, and these systems are 23 and 39 kJ/mol above the lowest minimum for  $\text{Cu}_2\text{EPh}^+$  with E = S and Se, respectively. In compound 7, we observed a  $\mu_2$ -bridging phenylthiolate ligand which matches approximately this trigonal planar geometry at the sulfur atom with  $\phi = 4^\circ$  and  $2\nu = 131.13(3)^\circ$ . Obviously, the energy needed to force this atom to planarity is overcome by steric effects.

The charge distribution around the chalcogen atom also affects the rotational angles of the phenyl group. As mentioned above, there is some charge delocalization from the chalcogen atom to the phenyl  $\pi$ -system in the HOMO. This can be interpreted as a +M-effect in terms of substituted aromatic systems. As can be seen from the phenyl region in the  $^1\text{H}$  NMR spectra, this charge delocalization decreases for heavier chalcogens, since chemical shifts increase for *ortho*- and *para*-protons going from sulfur to tellurium, comparing homologous compounds such as 1–3 or 15–17.

As a result of this charge delocalization, the donor capability of the  $\text{EPh}^-$  ligand is somewhat larger in the plane of the phenyl ring (compare Figure 13), and Cu–E bonds can be expected to be somewhat stronger in this direction. It should be noted that this effect does show structural consequences only if the Cu–E bond is relatively long (e.g., for tetrahedrally coordinated copper



**Figure 15.** Plot of inclination angles  $\phi$  against the respective Cu–E–Cu angles  $2\nu$  for compounds 1–18. Lines represent eq 1 for Cu–E–C angles  $\tau = 105^\circ$ ,  $110^\circ$ , and  $115^\circ$ .

atoms), since it is contrary to sterical effects, meaning the repulsive interaction between the copper atom and the *ortho*-hydrogen atom. We noted that for compound **16** a short and a long Cu–Se bond is observed, with the short one in plane with the phenyl ring. We suggest that this a manifestation of the charge delocalization. The same is true for the isostructural compound **17**.

## SUMMARY

We isolated 18 different trialkylphosphine-stabilized copper(I) phenylchalcogenolate complexes and characterized them by X-ray crystallography. The nuclearity of the complexes is mainly influenced by the size and amount of the phosphine ligand. In most cases, different phosphines result in different copper-chalcogen frameworks. In addition, the change of the chalcogen atom can also cause different structures, which is at least partly a steric effect, due to different atomic radii for different chalcogens. The Cu–E–C angles  $\tau$  were found to be relatively rigid, and electronic reasons were pointed out. As a result, for bridging chalcogenolate ligands a correlation between the inclination angle  $\phi$  of the E–C vector toward the respective Cu–E–Cu plane and the Cu–E–Cu angle  $2\nu$  is observed, since these three angles are related by their cosines:  $\cos \phi = \cos \tau / \cos \nu$ . Charge delocalization from the chalcogen atom to the phenyl  $\pi$ -system is only of minor importance for the overall molecular structure but has influence on bond lengths in the copper-chalcogen core.

## ASSOCIATED CONTENT

**S Supporting Information.** Experimental and computational details, tables of selected bond lengths and angles, histograms of distribution for Cu–E–C angles, crystallographic information in cif-file format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## DEDICATION

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

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