

# Copper-chalcogenide clusters stabilised with linear bidentate phosphine ligands †

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The bidentate phosphine ligands bis(diphenylphosphino)acetylene and 1,4-bis(diphenylphosphino)benzene have been found effectively to stabilise polynuclear copper/chalcogenide/chalcogenolate cores, acting as intramolecular bridges between copper centres. The clusters  $[\text{Cu}_{16}\text{Se}_4(\text{SePh})_8(\mu\text{-}1,4\text{-Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2)_4]$  **1** and  $[\text{Cu}_{25}\text{Te}_6(\text{TeBu}^n)_{13}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_6]$  **2** and the related binuclear complexes  $[(\text{Bu}^n\text{Te})\text{Cu}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_3\text{Cu}(\text{TeBu}^n)]$  **3** and  $[(\text{PhSe})\text{Cu}(\mu\text{-Ph}_2\text{PC}\equiv\text{C}\equiv\text{CPhPh}_2)_3\text{Cu}(\text{SePh})]$  **4** have been prepared and their molecular structures determined.

Bis(diphenylphosphino)acetylene, bis(diphenylphosphino)butadiyne and related compounds are well known to serve as phosphorus( $\sigma$ ) donor bridges between metal centres in coordination and organometallic compounds, often forming either dimeric<sup>1,2</sup> or polymeric complexes.<sup>3</sup> Thus, for example, the molecular complex  $[\text{Cl}_2\text{Pt}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_2\text{PtCl}_2]$  has been isolated where each metal centre is bridged by two bidentate phosphines,<sup>1b</sup> whereas in  $[\{\text{HgX}_2(\mu\text{-R}_2\text{PCCPR}_2)\}_n]$  ( $\text{X} = \text{halide}$ ) an infinite repeat of mercury atoms is linked by the  $\text{P}_2$  ligands.<sup>3b</sup> Alternatively, co-ordination to a metal site may occur through the alkyne functionality of these ligands in typical  $\eta^2$  ( $\pi$ ) fashion.<sup>4</sup>

In contrast to this chemistry, the co-ordination of  $\text{Ph}_2\text{PC}\equiv\text{CPhPh}_2$  on polymetallic centres remains relatively undeveloped.<sup>5</sup> There are reports where it and  $\text{Ph}_2\text{PC}\equiv\text{C}\equiv\text{CPhPh}_2$  have been shown to link two  $\text{M}_3$  cluster units.<sup>5f,i</sup> The relative weakness of the  $\text{P}\text{-C}_{\text{sp}}$  bond is such that thermal treatment of  $[\text{L}_n\text{M}_3\{\text{Ph}_2\text{P}(\text{C}\equiv\text{C})_x\text{PPh}_2\}_n\text{M}_3\text{L}_n]$  ( $x = 1$  or  $2$ ) complexes results in the formation of intermolecular  $\mu$ -diphenylphosphido groups and  $\sigma/\pi$   $\text{C}_2$  and  $\text{C}_4$  bridges between the polymetallic units.<sup>5i</sup> The compound  $\text{Ph}_2\text{PC}\equiv\text{CPhPh}_2$  may also intramolecularly bridge one metal–metal edge, as observed in  $\text{Re}_3$  and  $\text{Ir}_3\text{W}$  clusters.<sup>5e,f</sup>

Our research efforts have focussed on the synthesis of phosphine stabilised transition metal–chalcogenolate polynuclear complexes.<sup>6,7</sup> It has been possible to promote cluster condensation reactions, *via* the elimination of  $\text{ER}_2$  ( $\text{E} = \text{Se}$  or  $\text{Te}$ ) and the formation of high nuclearity metal/chalcogenide/chalcogenolate complexes.<sup>7</sup> Thus, for example, we were able to isolate and characterise structurally the anionic cluster  $[\text{Cu}_{50}\text{Te}_{17}(\text{TePh})_{20}(\text{PETPh}_2)_8]^{4-}$  from the light induced condensation of  $[\text{Cu}_6(\text{TePh})_6(\text{PETPh}_2)_5]$ .<sup>7</sup> The Group 12–16 complexes  $[\text{Hg}_{32}\text{Se}_{14}(\text{SePh})_{36}]$  and  $[\text{Cd}_{32}\text{Se}_{14}(\text{SePh})_{36}(\text{PPh}_3)_4]$  were also similarly prepared.<sup>6c</sup>

In this paper we present our results on the chemistry of copper–chalcogenolate complexes with  $\text{Ph}_2\text{PC}\equiv\text{CPhPh}_2$ ,  $\text{Ph}_2\text{PC}\equiv\text{C}\equiv\text{CPhPh}_2$  and 1,4-bis(diphenylphosphino)benzene ligands. The synthesis and structures of the clusters  $[\text{Cu}_{16}\text{Se}_4(\text{SePh})_8(\mu\text{-}1,4\text{-Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2)_4]$  **1** and  $[\text{Cu}_{25}\text{Te}_6(\text{TeBu}^n)_{13}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_6]$  **2** and the related binuclear complexes  $[(\text{Bu}^n\text{Te})\text{Cu}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_3\text{Cu}(\text{TeBu}^n)]$  **3** and  $[(\text{PhSe})\text{Cu}(\mu\text{-Ph}_2\text{PC}\equiv\text{C}\equiv\text{CPhPh}_2)_3\text{Cu}(\text{SePh})]$  **4** are described.

## Experimental

Standard Schlenk line techniques were employed throughout on a double manifold vacuum line with high purity dried nitrogen. Solvents for reactions and crystallisations were distilled

under nitrogen from appropriate drying agents prior to use: diethyl ether and tetrahydrofuran were dried over sodium–benzophenone and hexane and heptane were collected after refluxing over  $\text{LiAlH}_4$ . The deuterated solvent  $\text{C}_6\text{D}_6$  was dried by stirring over a  $\text{Na/K}$  alloy and distilling under reduced pressure. The silylated reagents  $\text{TeBu}^n(\text{SiMe}_3)^{6b}$  and  $\text{SePh}(\text{SiMe}_3)^{8}$  and the phosphines  $\text{Ph}_2\text{PC}\equiv\text{CPhPh}_2$  (from  $\text{LiC}\equiv\text{CLi}$ ),  $\text{Ph}_2\text{PC}\equiv\text{C}\equiv\text{CPhPh}_2$  (from  $\text{LiC}\equiv\text{CC}\equiv\text{CLi}$ ) and  $\text{C}_6\text{H}_4(\text{PPh}_2)_2$ -1,4 were each prepared according to literature methods.<sup>2g,9</sup>

The  $^{31}\text{P}\text{-}\{^1\text{H}\}$  spectra were acquired on a Bruker AC 250 instrument operating at 101.3 MHz,  $^{77}\text{Se}\text{-}\{^1\text{H}\}$  spectra on an AMX 300 spectrometer at an operating frequency of 57.2 MHz, and are referenced to the external standard  $\text{SeMe}_2$ .

## Syntheses

**[Cu<sub>16</sub>Se<sub>4</sub>(SePh)<sub>8</sub>(μ-1,4-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>4</sub>] 1.** Copper(I) chloride (0.20 g, 2.0 mmol) and  $\text{C}_6\text{H}_4(\text{PPh}_2)_2$ -1,4 (0.54 g, 1.2 mmol) were suspended in thf (40 mL). The compound  $\text{SePh}(\text{SiMe}_3)$  (0.5 mL, 2.0 mmol) was added with vigorous stirring and the murky solution gradually changed from colourless to light yellow to, after stirring overnight, orange. The solution was separated from the precipitate and allowed to stand for several days to produce orange, block-like crystals of **1**. Yield: 18% (Found: C, 49.39; H, 4.41. Calc. for  $\text{C}_{168}\text{H}_{136}\text{Cu}_{16}\text{P}_8\text{Se}_{12}\cdot 11\text{thf}$ : C, 49.31; H, 4.38%).

**[Cu<sub>25</sub>Te<sub>6</sub>(TeBu<sup>n</sup>)<sub>13</sub>(μ-Ph<sub>2</sub>PC≡CPhPh<sub>2</sub>)<sub>6</sub>] 2.** *Method 1.* Copper(I) chloride (0.12 g, 1.2 mmol) and  $\text{Ph}_2\text{PC}\equiv\text{CPhPh}_2$  (0.72 g, 1.8 mmol) were suspended in thf (20 mL) and  $\text{TeBu}^n(\text{SiMe}_3)$  (0.18 mL, 0.6 mmol) was added, followed by  $\text{Te}(\text{SiMe}_3)$  (0.07 mL, 0.3 mmol) to form a homogeneous red-brown solution. The reaction mixture was allowed to stand for 2.5 h and layered with hexane. Dark red crystals of compound **2** grew within several days at room temperature. Small amounts (<2%) of **3** (see below) invariably cocrystallised with **2** resulting in poor agreement of the chemical analyses. Yield: 65% (Found: C, 36.5; H, 3.77. Calc. for  $\text{C}_{208}\text{H}_{237}\text{Cu}_{25}\text{P}_{12}\text{Te}_{19}$ : C, 35.1; H, 3.59%).

*Method 2.* The compound  $\text{TeBu}^n(\text{SiMe}_3)$  (0.54 mL, 1.8 mmol) was added to a suspension of  $\text{CuCl}$  (0.18 g, 1.8 mmol) and  $\text{Ph}_2\text{PC}\equiv\text{CPhPh}_2$  (0.36 g, 0.9 mmol) in thf (10 mL). The resultant red-brown murky solution was filtered and layered with heptane. Red crystals of **2** (yield *ca.* 5%) cocrystallised with small amounts of the complex  $[\text{ClCu}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_3\text{CuCl}]^{1a}$  after several days.

**[(Bu<sup>n</sup>Te)Cu(μ-Ph<sub>2</sub>PC≡CPhPh<sub>2</sub>)<sub>3</sub>Cu(TeBu<sup>n</sup>)] 3.** Copper(I) chloride (0.30 g, 3 mmol) was suspended in thf (20 mL) with  $\text{Ph}_2\text{PC}\equiv\text{CPhPh}_2$  (1.5 equivalents). Addition of  $\text{TeBu}^n(\text{SiMe}_3)$  (0.9 mL, 4 mmol) resulted in the immediate formation of a deep gold

† Dedicated to Professor Alan Walker on the occasion of his retirement.

coloured, homogeneous solution. The solution was stirred for a few minutes and layered with hexane to afford yellow crystals of compound **3** within several days. Yield: 55% (Found: C, 61.75; H, 4.82. Calc. for  $C_{43}H_{39}CuP_3Te$ : C, 61.5; H, 4.68%).

**[(PhSe)Cu( $\mu$ -Ph<sub>2</sub>PC $\equiv$ CC $\equiv$ CPPh<sub>2</sub>)<sub>3</sub>Cu(SePh)] 4.** Copper(I) chloride (0.10 g, 1.0 mmol) and Ph<sub>2</sub>PC $\equiv$ C $\equiv$ CPPh<sub>2</sub> (0.63 g, 1.5 mmol) were stirred together in thf (40 mL). The compound SePh(SiMe<sub>3</sub>) (0.25 mL, 1.0 mmol) was added to yield a yellow, homogeneous solution. The volume was reduced to ca. 15 mL from which yellow crystals of **4** formed. Yield: 40% (Found: C, 67.9; H, 4.59. Calc. for  $C_{96}H_{70}Cu_2P_6Se_2 \cdot 5OC_4H_8$ : C, 67.9; H, 4.16%).

### X-Ray structural analyses

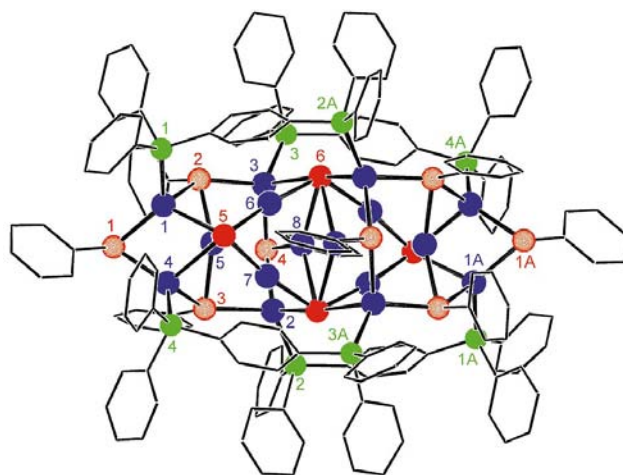
The selection and mounting of single crystals suitable for X-ray diffraction were carried out by immersing the air sensitive samples in perfluoropolyether oil (Riedel de Hen) and mounting a coated crystal on a glass pin set in a goniometer head, the oil setting upon cooling in a flow of N<sub>2</sub>. A single crystal X-ray structural analysis of compound **3** was performed on a STOE STADI IV four circle diffractometer using graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. Structural analyses of **1**, **2** and **4** were carried out on a STOE IPDS instrument (Mo-K $\alpha$ ) equipped with an imaging plate area detector and a rotating anode. Data were corrected for Lorentz-polarisation effects and structure solution and refinements were carried out using SHELXS 86<sup>10a</sup> and SHELXL 93<sup>10b</sup> software using direct methods techniques. Absorption corrections for **3** were applied with a series of  $\psi$  scans. No absorption correction was applied for complexes **1**, **2** and **4**. The weighting scheme employed was of the form  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  ( $a$ ,  $b$  = refined variables;  $P = \frac{1}{3}\max(F_o^2, 0) + \frac{2}{3}F_c^2$ ). All calculations were performed using a Silicon Graphics INDY computer. Molecular diagrams were prepared using the SCHAKAL 92 program.<sup>11</sup>

**Crystal data.** For **1**,  $C_{168}H_{136}Cu_{16}P_8Se_{12} \cdot 11C_4H_8O$ ,  $M = 5159.8$ , triclinic, space group  $P\bar{1}$ ,  $a = 17.196(7)$ ,  $b = 17.729(10)$ ,  $c = 20.697(12)$  Å,  $\alpha = 104.25(4)$ ,  $\beta = 93.76(4)$ ,  $\gamma = 116.11(4)^\circ$ ,  $U = 5381(5)$  Å<sup>3</sup>,  $T = 180$  K,  $Z = 1$ ,  $D_c = 1.592$  g cm<sup>-3</sup>,  $F(000) = 2576$ ,  $\mu = 3.604$  mm<sup>-1</sup>, 19 817 reflections measured, 12 775 unique (merging  $R = 0.0651$ ), 7383 with  $I > 2\sigma(I)$ . The final  $R$  was 0.0657 [ $wR(F^2) = 0.1617$ ] with a goodness of fit of 0.963. Eleven thf solvent molecules of crystallisation were located and refined isotropically (H atoms omitted).

For **2**,  $C_{208}H_{237}Cu_{25}P_{12}Te_{19}$ ,  $M = 7121.5$ , triclinic, space group  $P\bar{1}$ ,  $a = 17.688(4)$ ,  $b = 24.428(5)$ ,  $c = 30.419(6)$  Å,  $\alpha = 88.22(3)$ ,  $\beta = 84.90(3)$ ,  $\gamma = 79.41(3)^\circ$ ,  $U = 12 867(4)$  Å<sup>3</sup>,  $T = 200$  K,  $Z = 2$ ,  $D_c = 1.838$  g cm<sup>-3</sup>,  $F(000) = 6756$ ,  $\mu = 4.243$  mm<sup>-1</sup>, 51 547 reflections measured, 35 040 unique (merging  $R = 0.0439$ ), 25 619 with  $I > 2\sigma(I)$ . The final  $R$  was 0.0743 [ $wR(F^2) = 0.2095$ ] with a goodness of fit of 1.032. The Te–C and C–C (butyl) distances were refined with common values (within 3 e.s.d.s). Not all C atoms of disordered alkyl chains could be located in the Fourier difference map and phenyl rings were refined as rigid groups.

For **3**,  $C_{86}H_{78}Cu_2P_6Te_2$ ,  $M = 1679.6$ , monoclinic, space group  $C2/c$ ,  $a = 24.715(4)$ ,  $b = 13.785(3)$ ,  $c = 27.960(6)$  Å,  $\beta = 124.43(1)^\circ$ ,  $U = 7857(3)$  Å<sup>3</sup>,  $T = 200$  K,  $Z = 4$ ,  $D_c = 1.420$  g cm<sup>-3</sup>,  $F(000) = 3384$ ,  $\mu = 1.435$  mm<sup>-1</sup>, 9076 reflections measured, 8548 unique (merging  $R = 0.0349$  after a semiempirical  $\psi$  scan absorption correction), 7045 with  $I > 2\sigma(I)$ . The final  $R$  was 0.0392 [ $wR(F^2) = 0.0849$ ] with a goodness of fit of 1.032.

For **4**,  $C_{96}H_{70}Cu_2P_6Se_2 \cdot 5OC_4H_8$ ,  $M = 2054.9$ , tetragonal, space group  $P4_32_12$ ,  $a = 13.530(1)$ ,  $c = 54.462(10)$  Å,  $U = 9970(2)$  Å<sup>3</sup>,  $T = 203$  K,  $Z = 4$ ,  $D_c = 1.369$  g cm<sup>-3</sup>,  $F(000) = 4248$ ,  $\mu = 1.308$  mm<sup>-1</sup>, 21 415 reflections measured, 6410 unique (merging  $R = 0.0694$ ), 5627 with  $I > 2\sigma(I)$ . The final  $R$  was



**Fig. 1** Molecular structure of  $[Cu_{16}Se_4(SePh)_8(\mu-1,4-Ph_2PC_6H_4PPh_2)_4]$  **1**. Key: Cu, blue; Se<sup>2-</sup>, solid red; PhSe<sup>-</sup>, open red; P, green

0.0658 [ $wR(F^2) = 0.1715$ ] with a goodness of fit of 1.075 and an absolute structure parameter of 0.08(2).

CCDC reference number 186/1021.

### Results and Discussion

The chemistry of metal–selenolate and –tellurolate polynuclear complexes continues to progress at a rapid pace.<sup>12</sup> Recent reports have detailed the synthesis and structural characterisation of Group 12–16 nanoclusters<sup>6c,e,13</sup> and, more recently, Brennan and co-workers<sup>14</sup> have detailed new synthetic routes to ternary phase lanthanide/chalcogenido/chalcogenolato cluster complexes.

Work in our laboratories has focussed on the reactions of bis(silylated) chalcogen reagents with transition metal salts in the presence of ancillary tertiary phosphine ligands.<sup>15</sup> The reactions are driven by the generation and elimination of ClSiMe<sub>3</sub> and the formation of metal–chalcogen bonds. We have also reported that Group 12–16 high nuclearity metal/telluride/tellurolate cluster complexes may be formed by either: (i) photolytic condensation of smaller, phosphine stabilised copper–tellurolate polynuclear complexes<sup>7</sup> or (ii) the reaction of AgCl, dissolved in ether solvents with PR<sub>3</sub> ligands, with a combination of mono- and bis-silylated tellurium reagents.<sup>6e</sup> In an effort to expand this work, we set out to explore the related chemistry of copper–chalcogenolate complexes stabilised with bidentate phosphine ligands.

The 1 : 1 reaction of copper(I) chloride with SePh(SiMe<sub>3</sub>) and 0.6 equivalent of 1,4-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> led to the formation of  $[Cu_{16}Se_4(SePh)_8(\mu-1,4-Ph_2PC_6H_4PPh_2)_4]$  **1** as the only crystalline product, in moderate yields. The molecular structure of **1** is shown in Fig. 1. The cluster, which sits on a crystallographic inversion centre in the space group  $P\bar{1}$ , contains two  $\mu$ - and six  $\mu_3$ -SePh<sup>-</sup> groups as well as four selenide (Se<sup>2-</sup>) ligands, two of which are bonded in  $\mu_5$  and two in  $\mu_6$  fashion to the copper sites. The four bidentate phosphine ligands act exclusively as intramolecular bridges. The metal sites Cu(1)–Cu(4) exhibit near tetrahedral co-ordination geometries with Cu(1) and Cu(4) each bonded to the selenide ligand Se(5) [Se–Cu 2.563(3) and 2.768(3) Å respectively, Table 1] and selenolate Se(1) [Cu(1)–Se(1) 2.399(3), Cu(4)–Se(1) 2.386(2) Å]. As is usually observed in polymetallic chalcogenolate complexes, the  $\mu$ -Se(Ph)–Cu distances [average Se(1)–Cu 2.393(4) Å] are markedly shorter than their  $\mu_3$  [Se(2)–Se(4)] counterparts [average Se–Cu 2.499 Å]. Similarly, the average  $\mu_5$ -Se(5)–Cu bond length [2.496(6) Å] is slightly shorter than that for  $\mu_6$ -Se(6) [2.537(6) Å]. Atoms Cu(2) and Cu(3) also achieve tetrahedral co-ordination with two PhSe<sup>-</sup> [Se(3), Se(4) and Se(2), Se(4) respectively], one Se<sup>2-</sup> [Se(6(A)), Se(6)] and one phosphine ligand [P(2), P(3)]. The remaining metal sites within the cluster core

display either near trigonal planar [Cu(5), Cu(8); sum of the angles = 357.2, 359.8°] or linear [Cu(6), Cu(7); 172.4, 170.8°] co-ordination geometries.

There is no markedly short Cu...Cu contact (2.627–2.747 Å), consistent with a +1 oxidation state at the metal centres. The phosphine ligands, for their part, bridge copper centres separated by distances from 7.131 to 7.311 Å. Also noteworthy are the P–C<sub>ipso</sub>...C<sub>ipso</sub> angles of the linking C<sub>6</sub>H<sub>4</sub> bridges which deviate markedly from linearity (167.6–171.3°).

In a related reaction with an excess of Ph<sub>2</sub>PC≡CPh<sub>2</sub> the cluster [Cu<sub>25</sub>Te<sub>6</sub>(TeBu<sup>n</sup>)<sub>13</sub>(μ-Ph<sub>2</sub>PC≡CPh<sub>2</sub>)<sub>6</sub>] **2** is formed in good yields from the reaction of CuCl, TeBu<sup>n</sup>(SiMe<sub>3</sub>) and Te(SiMe<sub>3</sub>)<sub>2</sub> in a 4:2:1 ratio. Although yields are poorer, **2** may also be prepared from CuCl and TeBu<sup>n</sup>(SiMe<sub>3</sub>) (1:1) in an analogous method to that described for **1**, with 0.5 equivalent of Ph<sub>2</sub>PC≡CPh<sub>2</sub>. Clusters **1** and **2** are but sparingly soluble in ether solvents.

The cluster core of **2** is shown in Fig. 2. The molecule, which possesses a pseudo twofold rotation axis along the Te(2)–Cu(5) vector, consists of thirteen μ<sub>3</sub>-Bu<sup>n</sup>Te<sup>-</sup> and six μ<sub>6/7</sub>-Te<sup>2-</sup> sites and six Ph<sub>2</sub>PC≡CPh<sub>2</sub> ligands bonded to the 25 copper atoms. The latter, with the exception of Cu(5), Cu(10), Cu(15) and Cu(20) which form but three bonds each in near trigonal planar fashion (sum of the angles = 347–360 °C), all exhibit tetrahedral co-ordination. The alkanetellurolate ligands bond in μ<sub>3</sub> and μ<sub>4</sub> fashion [2.521(2)–2.967(2) Å] and the six Te<sup>2-</sup> [Te(4)–Te(7), Te(12), Te(15)] form bonding contacts to either six or

seven copper sites (Table 2). The combination of thirteen RTe<sup>-</sup> and six Te<sup>2-</sup> allows a +1 oxidation state to be assigned to the copper centres.

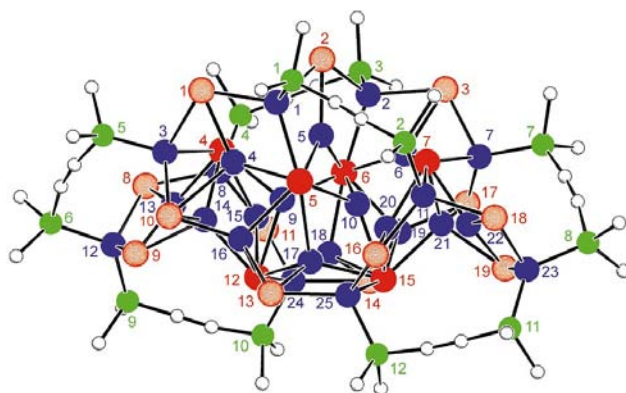
Although the ten copper sites at the cluster surface are each four-co-ordinate, atoms Cu(12) and Cu(23) are bonded to two Bu<sup>n</sup>Te<sup>-</sup> and two phosphine ligands whereas Cu(1)–Cu(3), Cu(7), Cu(8), Cu(11), Cu(24) and Cu(25) are bonded to two Bu<sup>n</sup>Te<sup>-</sup>, one Te<sup>2-</sup> and one end of a Ph<sub>2</sub>PC≡CPh<sub>2</sub> ligand. The distances spanned by the bidentate phosphine ligands range from 5.472 to 6.434 Å. The P–C<sub>sp</sub>–C<sub>sp</sub> angles of these ligands vary from nearly linear to markedly bent (178–168°) suggesting considerable strain about the latter centres. The Ph<sub>2</sub>PC≡CPh<sub>2</sub> ligands P(5), P(6) and P(7), P(8) span the shortest Cu...Cu vectors (5.47 and 5.63 Å respectively) and also exhibit the greatest P–C<sub>sp</sub>–C<sub>sp</sub> distortion. A similar, even greater ‘bending’ (150°) of the Ph<sub>2</sub>PC≡CPh<sub>2</sub> ligand was reported in the cluster [Re<sub>3</sub>H<sub>3</sub>(CO)<sub>10</sub>(μ-Ph<sub>2</sub>PC≡CPh<sub>2</sub>)] bridging a Re–Re distance of only 3.303(1) Å.<sup>5f</sup>

Chalcogenolate ligands exhibit a strong tendency to adopt a bridging *versus* terminal position in metal complexes.<sup>12</sup> Indeed, this is what makes them so useful in stabilising metal–chalcogen cluster cores. Arnold and co-workers<sup>16</sup> have demonstrated however that it is possible to ‘force’ a terminal co-ordination mode by increasing the steric effects of the alkyl chain on ER<sup>-</sup>. Alternatively, a terminal co-ordination mode can be achieved by blocking all additional sites about the metal centre. This

**Table 1** Selected bond lengths (Å) for compound **1**

Se(1)–Cu(4)	2.386(2)	Se(1)–Cu(1)	2.399(3)
Se(2)–Cu(5)	2.365(3)	Se(2)–Cu(3)	2.481(2)
Se(2)–Cu(1)	2.700(2)	Se(3)–Cu(5)	2.374(3)
Se(3)–Cu(2)	2.526(2)	Se(3)–Cu(4)	2.599(2)
Se(4)–Cu(8)	2.406(3)	Se(4)–Cu(3)	2.506(3)
Se(4)–Cu(2)	2.535(2)	Se(5)–Cu(7)	2.293(2)
Se(5)–Cu(6)	2.296(2)	Se(5)–Cu(5)	2.560(3)
Se(5)–Cu(1)	2.563(3)	Se(5)–Cu(4)	2.768(3)
Se(6)–Cu(6)	2.269(2)	Se(6)–Cu(7A)	2.277(2)
Se(6)–Cu(2A)*	2.583(3)	Se(6)–Cu(8)	2.596(3)
Se(6)–Cu(3)	2.741(3)	Se(6)–Cu(8A)	2.757(2)
Cu(1)–P(1)	2.238(4)	Cu(2)–P(2)	2.276(4)
Cu(3)–P(3)	2.282(4)	Cu(4)–P(4)	2.241(4)

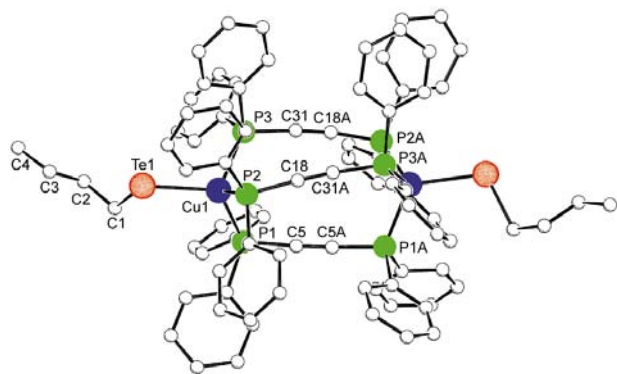
Symmetry transformation used to generate equivalent atoms: A  $-x, -y, -z$ .



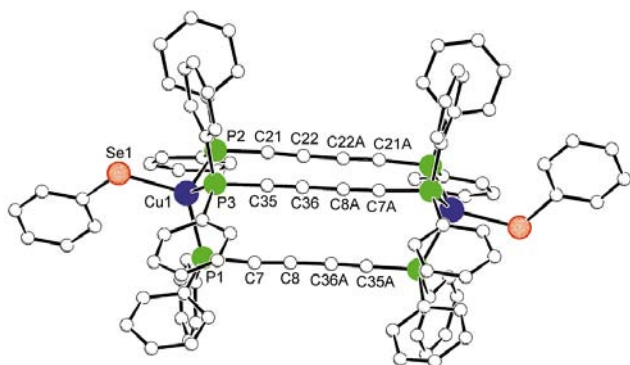
**Fig. 2** Molecular structure of [Cu<sub>25</sub>Te<sub>6</sub>(TeBu<sup>n</sup>)<sub>13</sub>(μ-Ph<sub>2</sub>PC≡CPh<sub>2</sub>)<sub>6</sub>] **2**. For clarity, the butyl chains and phenyl rings have been omitted and the atom centres are labelled with numbers only. Key: Cu, blue; Te<sup>2-</sup>, solid red; Bu<sup>n</sup>Te<sup>-</sup>, open red; P, green

**Table 2** Selected bond lengths (Å) for compound **2**

Te(1)–Cu(1)	2.610(2)	Te(1)–Cu(4)	2.660(2)	Te(11)–Cu(24)	2.642(2)	Te(12)–Cu(18)	2.571(2)
Te(1)–Cu(3)	2.669(3)	Te(2)–Cu(5)	2.556(2)	Te(12)–Cu(14)	2.642(2)	Te(12)–Cu(15)	2.690(2)
Te(2)–Cu(2)	2.622(2)	Te(2)–Cu(1)	2.691(2)	Te(12)–Cu(17)	2.780(2)	Te(12)–Cu(9)	2.793(2)
Te(3)–Cu(6)	2.624(2)	Te(3)–Cu(2)	2.637(2)	Te(12)–Cu(24)	2.811(2)	Te(12)–Cu(16)	2.852(2)
Te(3)–Cu(7)	2.670(2)	Te(4)–Cu(14)	2.638(2)	Te(13)–Cu(25)	2.588(2)	Te(13)–Cu(17)	2.637(2)
Te(4)–Cu(13)	2.677(2)	Te(4)–Cu(15)	2.686(2)	Te(13)–Cu(16)	2.641(2)	Te(14)–Cu(24)	2.580(2)
Te(4)–Cu(3)	2.819(2)	Te(4)–Cu(8)	2.827(2)	Te(14)–Cu(18)	2.645(2)	Te(14)–Cu(19)	2.669(2)
Te(4)–Cu(4)	2.872(3)	Te(4)–Cu(9)	2.933(2)	Te(15)–Cu(17)	2.580(2)	Te(15)–Cu(10)	2.680(2)
Te(5)–Cu(4)	2.592(2)	Te(5)–Cu(5)	2.645(2)	Te(15)–Cu(20)	2.682(2)	Te(15)–Cu(21)	2.697(2)
Te(5)–Cu(10)	2.705(2)	Te(5)–Cu(9)	2.763(2)	Te(15)–Cu(25)	2.783(2)	Te(15)–Cu(19)	2.813(2)
Te(5)–Cu(1)	2.787(2)	Te(5)–Cu(16)	2.860(2)	Te(15)–Cu(18)	2.861(2)	Te(16)–Cu(11)	2.596(2)
Te(5)–Cu(17)	2.940(2)	Te(6)–Cu(5)	2.627(2)	Te(16)–Cu(20)	2.618(2)	Te(16)–Cu(25)	2.624(2)
Te(6)–Cu(6)	2.648(2)	Te(6)–Cu(10)	2.712(2)	Te(17)–Cu(19)	2.512(2)	Te(17)–Cu(7)	2.598(2)
Te(6)–Cu(19)	2.734(2)	Te(6)–Cu(9)	2.763(2)	Te(17)–Cu(21)	2.839(2)	Te(18)–Cu(22)	2.589(2)
Te(6)–Cu(2)	2.796(2)	Te(6)–Cu(18)	2.842(2)	Te(18)–Cu(23)	2.662(2)	Te(18)–Cu(21)	2.700(2)
Te(7)–Cu(22)	2.633(2)	Te(7)–Cu(6)	2.651(2)	Te(19)–Cu(11)	2.602(2)	Te(19)–Cu(23)	2.634(2)
Te(7)–Cu(20)	2.664(2)	Te(7)–Cu(21)	2.691(2)	Te(19)–Cu(22)	2.648(2)	Cu(9)–P(1)	2.266(5)
Te(7)–Cu(11)	2.792(2)	Te(7)–Cu(7)	2.855(2)	Cu(2)–P(3)	2.259(5)	Cu(3)–P(5)	2.216(4)
Te(8)–Cu(13)	2.593(2)	Te(8)–Cu(8)	2.628(2)	Cu(7)–P(7)	2.224(4)	Cu(8)–P(4)	2.238(5)
Te(8)–Cu(12)	2.643(2)	Te(9)–Cu(13)	2.622(2)	Cu(11)–P(2)	2.244(4)	Cu(12)–P(9)	2.252(6)
Te(9)–Cu(14)	2.654(2)	Te(9)–Cu(12)	2.677(2)	Cu(12)–P(6)	2.285(6)	Cu(23)–P(11)	2.259(5)
Te(10)–Cu(16)	2.567(2)	Te(10)–Cu(3)	2.716(3)	Cu(23)–P(8)	2.274(4)	Cu(24)–P(10)	2.246(5)
Te(10)–Cu(14)	2.888(2)	Te(10)–Cu(4)	2.967(3)	Cu(25)–P(12)	2.247(4)		
Te(11)–Cu(15)	2.584(2)	Te(11)–Cu(8)	2.602(2)				



**Fig. 3** Molecular structure of  $[(\text{Bu}^n\text{Te})\text{Cu}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_3\text{Cu}(\text{TeBu}^n)]_2$  **3**



**Fig. 4** Molecular structure of  $[(\text{PhSe})\text{Cu}(\mu\text{-Ph}_2\text{PC}\equiv\text{CC}\equiv\text{CPhPh}_2)_3\text{Cu}(\text{SePh})]_2$  **4**

is borne out with the synthesis of  $[(\text{Bu}^n\text{Te})\text{Cu}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_3\text{Cu}(\text{TeBu}^n)]_2$  **3** and  $[(\text{PhSe})\text{Cu}(\mu\text{-Ph}_2\text{PC}\equiv\text{CC}\equiv\text{CPhPh}_2)_3\text{Cu}(\text{SePh})]_2$  **4** (Figs. 3 and 4, Tables 3 and 4) from  $[\text{ClCu}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_3\text{CuCl}]$ .<sup>1a</sup> Complex **3** sits on a crystallographic twofold rotation axis that bisects the vectors C(5)–C(5A) and Cu(1)–Cu(1A). The two tetrahedral copper centres in **3** are each bonded to three phosphorus and one tellurium atoms. The three Cu–P distances vary little [2.2789(11)–2.3042(11) Å], the Te–Cu [2.5807(6) Å] and Te–C bond lengths are typical for this bonding arrangement<sup>6b</sup> and the two butyl chains adopt a relative *trans* orientation in the solid state. Complex **3** is related to the platinum–selenium dimeric species  $[(\eta^2\text{-Z}_2\text{C}_2\text{Se}_2)\text{Pt}(\mu\text{-Ph}_2\text{PC}\equiv\text{CPhPh}_2)_2\text{Pt}(\eta^2\text{-Se}_2\text{C}_2\text{Z}_2)]$  (Z = CF<sub>3</sub> or CO<sub>2</sub>CH<sub>3</sub>) reported by Bolinger and Rauchfuss.<sup>17</sup>

The partially eclipsed arrangement of the three Ph<sub>2</sub>PC≡CPhPh<sub>2</sub> ligands in compound **3** is such that the Cu(μ-Ph<sub>2</sub>PC≡CPhPh<sub>2</sub>)<sub>3</sub>Cu moiety displays a helical twist, with a distinct dihedral angle between the planes defined by P(2)–Cu(1)–Cu(1A) and P(3A)–Cu(1A)–Cu(1) of 23.6°. This is less evident with the C<sub>4</sub> linkages in **4** (dihedral angle = 5.5°, see below). The Cu⋯Cu separation (6.403 Å) in **3** lies in the range of the longer distances observed in **2**.

The preparation of compound **4** involves a similar reaction as for **3** with the bidentate phosphine Ph<sub>2</sub>PC≡CC≡CPhPh<sub>2</sub> and SePh(SiMe<sub>3</sub>). As observed for **3**, the molecule consists of two metal–chalcogenolate centres bridged by three P<sub>2</sub> ligands (Cu⋯Cu 9.014 Å), each centre crystallographically related by a twofold rotation axis bisecting the C(22)–C(22A) and Cu(1)–Cu(1A) vectors. The chalcogenolate ligands in **4** adopt a *trans* orientation relative to each other with a Cu–Se bond length of 2.420(1) Å. Whereas crystals of **3** are unstable in solution, it proved possible to obtain <sup>31</sup>P-<sup>1</sup>H and <sup>77</sup>Se-<sup>1</sup>H NMR spectra of **4**. A sharp singlet (δ –26.1) is observed in the <sup>31</sup>P-<sup>1</sup>H spectrum although no J<sub>PSe</sub> satellites are evident. The <sup>77</sup>Se-<sup>1</sup>H spectrum consists of a quartet centred at δ –34.7 (J<sub>PSe</sub> = 34 Hz) illustrating the equivalence of the three phosphorus centres in solution.

**Table 3** Selected bond lengths (Å) and angles (°) for compound **3**

Te(1)–C(1)	2.171(5)	Te(1)–Cu(1)	2.5807(6)
Cu(1)–P(1)	2.2789(11)	Cu(1)–P(2)	2.2803(11)
Cu(1)–P(3)	2.3042(11)	P(1)–C(5)	1.776(3)
P(1)–C(6)	1.833(4)	P(1)–C(12)	1.834(4)
P(2)–C(18)	1.765(4)	P(2)–C(19)	1.826(4)
P(2)–C(25)	1.831(4)	P(3)–C(31)	1.773(4)
P(3)–C(38)	1.832(4)	P(3)–C(32)	1.832(4)
C(5)–C(5A)*	1.199(7)	C(18)–C(31A)	1.214(5)
C(1)–Te(1)–Cu(1)	106.99(13)	P(1)–Cu(1)–P(2)	107.65(4)
P(1)–Cu(1)–P(3)	107.55(4)	P(2)–Cu(1)–P(3)	104.23(4)
P(1)–Cu(1)–Te(1)	118.32(3)	P(2)–Cu(1)–Te(1)	107.03(3)
P(3)–Cu(1)–Te(1)	111.12(3)	C(5A)–C(5)–P(1)	177.31(12)
C(31A)–C(18)–P(2)	172.8(3)		

Symmetry transformation used to generate equivalent atoms: A –x, y, –z + ½.

**Table 4** Bond lengths (Å) and angles (°) for compound **4**

Cu(1)–P(1)	2.307(2)	Cu(1)–P(2)	2.325(2)
Cu(1)–P(3)	2.336(2)	Cu(1)–Se(1)	2.420(1)
Se(1)–C(1)	1.907(7)	P(1)–C(7)	1.763(8)
P(1)–C(9)	1.804(7)	P(1)–C(15)	1.829(8)
C(7)–C(8)	1.218(12)	C(8)–C(36A)	1.389(13)
P(2)–C(21)	1.768(8)	P(2)–C(23)	1.832(8)
P(2)–C(29)	1.845(8)	C(21)–C(22)	1.221(11)
C(22)–C(22A)*	1.35(2)	P(3)–C(35)	1.776(8)
P(3)–C(43)	1.831(7)	P(3)–C(37)	1.836(8)
C(35)–C(36)	1.201(11)		
P(1)–Cu(1)–P(2)	111.03(8)	P(1)–Cu(1)–P(3)	102.31(8)
P(2)–Cu(1)–P(3)	108.72(8)	P(1)–Cu(1)–Se(1)	121.86(6)
P(2)–Cu(1)–Se(1)	108.84(6)	P(3)–Cu(1)–Se(1)	102.93(6)
C(1)–Se(1)–Cu(1)	113.2(2)	C(8)–C(7)–P(1)	174.2(7)
C(7)–C(8)–C(36A)	177.8(8)	C(22)–C(21)–P(2)	174.3(7)
C(21)–C(22)–C(22A)	177.3(5)	C(36)–C(35)–P(3)	178.8(7)
C(35)–C(36)–C(8A)	178.1(8)		

Symmetry transformation used to generate equivalent atoms: A –y, x, –z.

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