Gabriele Kociok-Köhn, Mary F. Mahon*, Kieran C. Molloy* and Anna L. Sudlow

Synthesis and structures of Cu-Cl-M adducts (M=Zn, Sn, Sb)

Abstract: The novel bimetallic adducts [(Ph₃P)₂CuCl]₂.ZnCl₂ (1), [(Me₃P)CuCl]₂.ZnCl₂ (2), [(Me₃P)₂Cu]⁺[Me₃P]Cl⁻ (3), (Ph₃P)₂CuCl.SbCl₃ (4), (Me₃P)₂CuSnCl₃ (5), [(Ph₃P)₂CuCl.SbCl₃]₂ (6) and (Ph₃P)₂CuCl.SbCl₄ (7) have been synthesized from combinations of R₃P, CuCl and one of ZnCl₂, SnCl₂ or SbCl₃, and their structures were determined. [(Me₃P)₂Cu⁺[HPMe₃]₂[Sb₂Cl₉]⁻ (8) and [(Me₃P)₄Cu⁺[(Me₃P)₂SbCl₄] (9) have been isolated as minor by-products from the reaction of Me₃P, CuCl and SbCl₄, and their structures were also determined.

Keywords: antimony; bimetallic; chloride; copper; tin; X-ray crystallography; zinc.

*Corresponding authors: Mary F. Mahon, (for crystallographic correspondence), Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK, e-mail: m.f.mahon@bath.ac.uk; and Kieran C. Molloy, (for general correspondence), Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK, e-mail: k.c.molloy@bath.ac.uk.

Gabriele Kociok-Köhn and Anna L. Sudlow: Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

Introduction

We have an ongoing interest in the chemistry of precursors for ternary and quaternary multimetal chalcogenides such as Cu₂SnE₃, CuSbE₂ and Cu₂ZnSnE₄ (E=S, Se), which are currently being actively studied as novel energy materials incorporating low-cost, earth-abundant metals (Kociok-Köhn et al., 2013). For example, Cu₂ZnSnS₄ (CZTS) or the related Cu₂ZnSnSe₄ (CZTSe) has been used as an absorber layer in photovoltaic cells with efficiencies that have now exceeded 11% (Abermann, 2013; Colombara et al., 2012). CuSbS₂ is, like the widely exploited CuInS₂, part of the I-III-VI₂ class of semiconductors with a chalcopyrite structure. CuSbS₂ is a direct semiconductor with a band gap of 1.5 eV and as such is an ideal candidate for use as a solar absorber layer in a thin-film solar cell (Lazcano et al., 2001; Dufton et al., 2012; Temple et al., 2012), while the price of antimony is considerably lower than that of indium (Manolache et al., 2007). However, unlike CZTS/Se, this absorber layer is not, as yet, widely investigated (Nair et al., 2005; Manolache and Duta, 2007), and to our knowledge, no efficiencies for cells with CuSbS₂ absorber layers have been reported. Cu₂SnS₄ is an example of a ternary material with a high optical absorption coefficient (ca. 10⁴ cm⁻¹) (Guan et al., 2013) and a band gap in the range 1.00–1.19 eV (Su et al., 2012; Guan et al., 2013; Wang et al., 2013) from which solar cells with efficiencies of ca. 2.5% have been fabricated (Chino et al., 2012; Koike et al., 2012). Cu₂SnSe₂ has also been used as an intermediate in the synthesis of CZTS nanoparticles (Park et al., 2013).

One of the major challenges in the materials chemistry of these systems is the deposition of thin films from appropriate precursors, particularly in a dynamic methodology such as chemical vapor deposition (CVD), which allows for relatively rapid, large-scale coatings to be fabricated. The dominant problem is matching the decomposition profiles of two or three precursors such that the correct stoichiometry is achieved. Indeed, with regard to CZTS, although a number of routes to thin films via spray pyrolysis (Nakayama and Ito, 1996), sulfurization of electrodeposited metal precursors (Kurihara et al., 2009), non-vacuum electroplating (Ennaoui et al., 2009), spin coating (Yeh et al., 2009), pulsed laser deposition (Moriya et al., 2007) and photochemical deposition (Moriya et al., 2006), sputtering (Ito and Nakazawa, 1988) and co-evaporation (Tanaka et al., 2006) have been reported, there have only been two reports of a successful CVD route to this material (Ramasamy et al., 2012; Kociok-Köhn et al., 2013).

One way in which this problem could be mitigated is by the use of precursors that embody more than one metal in the correct relative ratio in a single precursor, e.g., Cu₂Zn, Cu₂Sn, Cu₂Sb, which would reduce the total number of precursors required in any deposition process. However, to our knowledge, relatively few systems of this type are known (e.g., Nayek et al., 2008), particularly when the need for simplicity (to offer the best chance of good volatility and/or solubility) is also considered. We have thus become interested in the synthesis of simple mixed-metal halide adducts that may provide an entry point into this area of chemistry. There are just three reported molecular structures involving the Cu-X-Sb (X=halogen) linkage, and all involve the [SbF₆]⁻ anion (Gardberg and Ibers, 2001; Manson et al., 2009; Nakajima et al., 2011). The Cu-X-Sn
system is even rarer with only two cited examples (Veith et al., 1989; Han et al., 2009), and although there are 11 structures that incorporate the Cu-X-Zn moiety, all but two (Mandal et al., 1988; Nakamura et al., 2001) of these are based on coordinated [ZnCl₂]²⁻ anions (Mandal et al., 1988; Zang et al., 1990; Gou et al., 1992; Prins et al., 1996; Gladkikh et al., 1997; Martin et al., 1998; Curtis and Gladkikh, 2000; Pryma et al., 2003; Shevchenko et al., 2005). Note that framework, rather than molecular, systems such as [Cu₃Zn₄Cl₁₁]⁺ are known (Martin et al., 1998). In the light of this, we now report the synthesis and structural characterization of novel molecular examples of each of these systems [Cu/Zn, Cu/Sn, Cu/Sb].

Results and discussion

Cu-Zn bimetallic systems

[(Ph₃P)₂CuCl]₂ZnCl₂ (1) was synthesized following a literature method for the synthesis of (Ph₃P)₂CuInCl₄ (Margulieux et al., 2010) by direct reaction of ZnCl₂ and (Ph₃P)₂CuCl in toluene. Although the initial synthesis involved reagents in a 1:1 stoichiometry, the resulting product always formulated as Cu₂Zn; as a result, the synthetic procedure was modified to improve the yield. Similarly, [(Me₃P)CuCl]₂ZnCl₂ (2) and [(Me₃P)₄Cu]⁺[(Me₃P)₂CuCl₂ZnCl₂]⁻ (3) were synthesized using a similar route, from ZnCl₂, CuCl and Me₃P at 60°C in toluene without prior formation and isolation of (Me₃P)₂CuCl. Although 2 retains the 2Cu:Zn ratio seen in 1, it contains less phosphine than the 2Cu:Zn ratio seen in 1, in which the P:Cu:Zn ratio reflects that of the reagents (Scheme 1). In comparison with 1, the ZnCl₄ unit is less regular, approximately orthogonal as a result of the tetrahedral geometry of the chlorines in [ZnCl₄]²⁻ [∠ range: 92.154(16)°–129.91(2)°], and additionally, the bulky phosphines attached to each of the two ions.

The structure of 1 is shown in Figure 1 and comprises what can viewed as a [ZnCl₄]²⁻ anion bridging two [(Ph₃P)₂Cu]⁺ cations in a μ₁, κ² manner; that is, the anion bridges two copper centers and simultaneously acts as a bidentate chelating ligand to each of them. The two unique Zn-Cl bonds [2.2709(5), 2.2902(5) Å] are close in length and shorter than the two Cu-Cl bonds [2.4555(5), 2.4535(5) Å], whereas each metal adopts a tetrahedral coordination sphere with significant distortion due to the chelating nature of the chlorines in [ZnCl₄]²⁻ [∠ range: 101.647(16)°–123.294(17)°], and additionally, the bulky phosphines attached to the copper [∠ range: 92.154(16)°–129.91(2)°]. The two CuCl₂Zn rings, which share a common zinc center, are planar and are twisted 75.52(1)° with respect to each other.

Surprisingly, in 2, which incorporates a less bulky phosphine, the Cu₂Zn stoichiometry is retained, but copper only coordinates one group 15 donor and adopts a trigonal planar coordination (Figure 2). However, rather than forming a discrete molecular entity, the nominal [ZnCl₄]²⁻ now acts in a μ₂-briding mode to four separate copper centers and coordinates in a monodentate mode to each. The resulting structure is that of a one-dimensional polymer, in which eight-membered Zn₂Cu₂Cl₄ rings join at a common zinc center, with alternate rings being approximately orthogonal as a result of the tetrahedral geometry at zinc. In comparison with 1, the ZnCl₄ unit is less regular, having two short [2.2563(6), 2.2547(6) Å] and two longer [2.2927(6), 2.2885(6) Å] Zn-Cl bonds. Similarly, the Cu-Cl bonds [2.2688(6), 2.2639(6), 2.370(6), 2.3849(6) Å] and Cu-P bonds [2.1913(6), 2.1772(6) Å] are shorter and less symmetric than in 1, although to some extent this will be a natural result of the lower coordination number at copper.

\[
\text{ZnCl}_2 + 2 (\text{Ph}_3\text{P})_2\text{CuCl} \xrightarrow{\text{toluene, 80°C, 4 h}} [(\text{Ph}_3\text{P})_2\text{CuCl}]_2\text{ZnCl}_2 (1)
\]

\[
\text{ZnCl}_2 + 2 \text{CuCl} + 4 \text{Me}_3\text{P} \xrightarrow{\text{toluene, 60°C, 1 h}} [(\text{Me}_3\text{P})\text{CuCl}]_2\text{ZnCl}_2 (2)
\]

\[
\text{ZnCl}_2 + 2 \text{CuCl} + 6 \text{Me}_3\text{P} \xrightarrow{\text{toluene, 60°C, 1 h}} [(\text{Me}_3\text{P})_4\text{Cu}]^+[(\text{Me}_3\text{P})_2\text{CuCl}_2\text{ZnCl}_2]^- (3)
\]

Scheme 1
from its chelating role, the ZnCl₄ tetrahedron in 2 becomes markedly more regular [∠ range: 106.16(2)°–112.64(3)°]. To our knowledge, this polymeric arrangement is unique, with the closest comparison being that of the framework structure of [H₃NMe⁺][Cu₂Zn₂Cl₇]⁻ (Martin et al., 1998).

The ionic product 3, which results from a protocol that involves a larger quantity of phosphine than in the synthesis of 2, retains a 2Cu:Zn ratio but is now formulated as a separated cation/anion pair: [Me₃P]⁺[(Me₃P)₂CuZnCl₄]⁻ (Figure 3). Although the tetrahedral cation is unremarkable, the anion can be viewed as half of that seen in 1, but with differences. Whereas formally the anion can be viewed as [ZnCl₄]²⁻ bonded to [(Me₃P)₂Cu]⁺ by analogy to 1, there is now marked asymmetry to the Zn-Cl...
bonds with those to the terminal halogens being shorter [2.2458(7), 2.2387(7) Å] than those to the bridging chlorines [2.3266(6), 2.3397(7) Å], whereas the Cu-Cl bonds are also less symmetrical than in \( \text{I} \) [2.5024(7), 2.4282(7) Å]; moreover, the resulting CuCl\( \text{Zn} \) ring is no longer planar. In comparison with \( \text{II} \), the Cu-P bonds in the anion are longer [2.2227(7), 2.2255(7) Å]; Cl(1)-Zn-Cl(2) 96.70(2), Cl(1)-Cu(2)-Cl(2) 90.00(2), Cl(1)-Cu(2)-P(1) 105.53(3), Cl(1)-Cu(2)-P(2) 104.60(3), Cl(2)-Cu(2)-P(1) 107.26(3), Cl(2)-Cu(2)-P(2) 106.00(3), P(1)-Cu(2)-P(2) 134.51(3), Zn-Cl(1)-Cu(2) 82.45(2), Zn-Cl(2)-Cu(2) 83.81(2)°.

**Cu-Sn bimetallic systems**

Analogous reactions involving SnCl\(_4\), and either preformed (Ph\(_3\)P)\(_2\)CuCl or in a one-pot reaction with CuCl/Me\(_3\)P yielded the Cu-Sn heterobimetallic species 4 and 5 (Scheme 2).

**Scheme 2**

\[
\begin{align*}
\text{SnCl}_2 + (\text{Ph}_3\text{P})_2\text{CuCl} & \quad \text{toluene, } 80°C, \text{N}_2 \quad (\text{Ph}_3\text{P})_2\text{CuCl} \cdot \text{SnCl}_2 \\
\text{SnCl}_2 + \text{CuCl} + 2\text{Me}_3\text{P} & \quad \text{toluene, } 60°C, \text{N}_2 \quad (\text{Me}_3\text{P})_2\text{CuSnCl}_3
\end{align*}
\]

Compound 4 is a neutral 1:1 adduct (Figure 4) and is related to both \( \text{I} \) (but as an equivalent 1:1, rather than 2:1, adduct) and \( \text{III} \) (as a neutral equivalent). Compound 4 can be viewed as an [SnCl\(_3\)]\(^-\) anion coordinating a [(Ph\(_3\)P)\(_2\)Cu\(^+\)] cation, by analogy with \( \text{I} \) and \( \text{III} \), but it is with the latter that the structural similarities are most striking. The Sn-Cl bonds divide into a short terminal [2.4562(12) Å] and longer bridging bonds to the \( \mu_2\)-Cl [2.5402(10), 2.5680(11) Å], while the two Cu-Cl bonds [2.4516(11), 2.5052(12) Å] are asymmetric and closely parallel those in \( \text{III} \), and the Cu-P bonds err marginally to the shorter side of those in \( \text{I} \) [2.2448(11), 2.2534(12) Å]; like \( \text{III} \), the CuCl\(_2\)Sn ring is non-planar. The geometry at copper is a distorted tetrahedron, with an angle range that, not surprisingly, resembles that for \( \text{I} \) [\( \angle \text{range: } 88.67(4)-135.81(4)\)°]. The [SnCl\(_3\)]\(^-\) is trigonal pyramidal with a vacant area above the metal for a lone electron pair. What is interesting about the anion/cation relationship here, which is not seen in \( \text{I} \) (but is relevant to the antimony compound \( \text{IV} \), below), is the orientation of the phenyl ring attached to P(2) [C(19)-C(24)] with respect to tin (Figure 4). This ring sits above tin with Sn-C distances of 3.647(4)–4.043(4) Å and a Sn-ring centroid separation of 3.585 Å, distances that reflect a much weaker \( \pi \)-interaction than seen in examples where a more cationic tin is bonded to aromatic rings [usually, but not exclusively, solvent molecules (Probst et al., 1990) in [MX\(_4\)]\(^-\) salts, M=B, X=C\(_6\)F\(_5\), (Schaefer et al., 2011), M=Al, X=Cl (Rodesiler et al., 1975; Weininger et al., 1979; Schmidbaur et al., 1989a,b,c, 1990b, 1991; Frank, 1990a,b), M=Ga, X=Cl (Frank, 1990c), where the Sn-ring centroid is ca. 2.6 Å. It is similar to that in in [Sn[S(\text{OPh})\(_2\)]\(_2\)]\(^-\), where, as in 4, the aromatic ring is part of an ancillary ligand (Sn-ring centroid 3.655 Å) (Jefferts et al., 1980). Interestingly, although all the C-C bonds within the C(19)-C(24) ring are equal within experimental error, those involving C(19), which is closest to tin [Sn(\text{C}(19)-3.647(4); C(19)-C(20) 1.393(6), C(19)-C(24) 1.398(6) Å], C(24) [Sn(\text{C}(24) 3.673(4) Å] and C(20) [Sn(\text{C}(20) 3.813(4); C(20)-C(21) 1.392(6) Å], err on the long side compared to the C-C bonds associated with longer Sn-C separations [1.372(6)-1.378(6) Å]. A more general review of p-block/arene compounds is available for the interested reader (Schmidbaur and Schier, 2008).

In contrast, the one-pot reaction involving Me\(_3\)P but retaining the reagent stoichiometry used to generate 4...
yields complex 5, which incorporates a direct Sn-Cu bond (Figure 5). Compound 5 can again be viewed as a [SnCl₃]⁻ anion coordinating a [(Ph₃P)₃Cu]^+ cation, but now coordination is via tin as a 2e donor rather than through halide bridges. As a consequence, there is an additional phosphine donor in 5 compared to 4 to maintain a tetrahedral geometry at copper. The Sn-Cu bond, which is not common, lies in the range 2.5662(14)–2.6160(15) Å across four independent molecules in the asymmetric unit and is longer than in Ar(SiMe₃)SnCu(SiMe₃) (Ar = C₆H₃Mes₂-2,6) [2.4992(5)Å] (Klett et al., 1999) and MeB[3-(CF₃)Pz]₃CuSn(Cl) (Bn₂ATI) (Pz = pyrazolyl, Bn₂ATI = N-benzyl-2-(benzylamino)-troponiminate) [2.4540(4)Å] (Dias et al., 2005), both of which incorporate Sn(II):→Cu(I) bonds, and that of a Sn(IV)-Cu(I) complex, Ph₃SnCu(LPr) [LPr=1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)] [2.469(5) Å] (Bhattacharyya et al., 2008). The tetrahedral geometries at both tin and copper are largely unexceptional, save for the slightly narrower range of Cl-Sn-Cl in 5 [95.75(13)°–96.39(12)°] compared to 4 [85.40(3)°–92.89(4)°], which may reflect the weak π-interaction in the latter.

Figure 5 One of four similar molecules that constitute the asymmetric unit of 5 showing the labeling scheme used. Thermal ellipsoids are at the 40% probability level; hydrogen atoms have been omitted for clarity. Selected geometric data: Sn(1)-Cu(1) 2.5997(14), Sn(1)-Cl(1) 2.435(3), Sn(1)-Cl(2) 2.426(3), Sn(1)-Cl(3) 2.444(3), Cu(1)-Cl(1) 2.264(3), Cu(1)-Cl(2) 2.242(3), Cu(1)-P(1) 2.250(3) Å; Cu(1)-Sn(1)-Cl(1) 120.33(9), Cu(1)-Sn(1)-Cl(2) 124.33(9), Cu(1)-Sn(1)-Cl(3) 95.89(14), Sn(1)-Cu(1)-P(1) 105.55(10), Sn(1)-Cu(1)-P(2) 101.99(8), P(1)-Cu(1)-P(2) 113.22(14), P(1)-Cu(1)-P(3) 117.41(15), P(2)-Cu(1)-P(3) 116.68(13)°.

Cu-Sb bimetallic systems

Following the approaches described above for Cu-Cl-Zn and Cu-Cl-Sn, Cu-Sb-Cl adducts were prepared similarly (Scheme 3):

When a 1:1 reaction stoichiometry is used, the product (6) is a 1:1 adduct, which, in keeping with the earlier discussions, can be thought of as the [SbCl₄]⁻ anion coordinated to a [(Ph₃P)₂Cu]⁺ cation. In the solid state, the molecule forms chlorine-bridged dimers to generate a five-coordinate square pyramidal geometry at antimony (r=0.13) (Addison et al., 1984), while the familiar distorted tetrahedral geometry [∠ range: 81.91(2)°–124.46(3)°] is maintained at copper (Figure 6). However, bond length analysis suggests that the anion/cation association is the least appropriate description in this case. Thus, Cu-Cl(I) is the shortest of the Cu-Cl distances in the (Ph₃P)₂Cu complexes studied [2.3129(7) Å], whereas the bond to the μ₂-Cl(2) is notably elongated [3.0070(9) Å]. Similarly, Cl(2) forms a short bond to antimony [2.3899(7) Å] and a much
weaker bridging bond to copper [3.0070(9) Å]. Thus, loose chlorine-bridged association between neutral (Ph3P)2CuCl and SbCl3 units is a more appropriate description here. Of the three chlorine atoms bonded to antimony, two are terminal [Sb-Cl(3) 2.3875(8); Sb-Cl(4) 2.3474(8) Å], one is μ2-bridging between Sb and Cu [Cl(2)] and one is μ3-bridging between two Sb atoms and one Cu atom [Cl(1)]. The weakness of the association between the heterometal units is reflected in the very short Sb-Cl(2) bond, which is very similar in length to the two terminal Sb-Cl bonds; dimerization by μ2-Cl bridges between antimony centers is also weak [Sb-Cl(1′) 3.2106(6) Å]. The Cu-P distances are similar to those in 1 [2.2668(8), 2.2701(8) Å].

In contrast, when an excess of (Ph3P)2CuCl is used in the reaction protocol, monomeric [(Ph3P)3CuCl.SbCl3] (7) is obtained (Figure 7). Compound 7 can be viewed as a [SbCl4]- anion coordinated in a monodentate fashion to [(Ph3P)3Cu]+ via a μ2-Cl bridge. The Cu-Cl bond [2.4240(9) Å] is similar to those in 1 and 4 and elongated with respect to Cu-Cl(1) in 6, whereas Sb-Cl(1) shows some lengthening [2.8005(9) Å] with respect to the three terminal Sb-Cl bonds [2.4473(10), 2.3549(11), 2.3474(10) Å] as a result of its bridging role; the four halogens then are more closely linked to antimony than copper. In addition to the μ2-Cl, tetrahedral coordination at copper is completed by three Cu-P bonds, each of which is longer [2.3402(10), 2.3532(9), 2.3244(10) Å] than in the bis-triphenylphosphine complexes 1 and 4, plausibly due to the steric crowding at copper from the three bulky donors. However, what is most interesting about this monomeric species is the role played by aromatic ring C(49)-C(54), which sits below antimony [Sb-C 3.468(4)–3.811(4); Sb-ring centroid 3.3323 (3) Å] in a manner analogous to that seen in
the tin complex 4, generating a five-coordinated square-pyramidal geometry at antimony, with apical Cl(4) trans to the vacant space presumably occupied by the lone pair on Sb(III). Interactions between aromatic rings and antimony – so-called Menshutkin complexes (Schmidbaur and Schier, 2008) – have been previously reported in the structures of, for example, SbCl₃‧Et₃C₆ (Schmidbaur et al., 1987), SbBr₃‧9,10-dihydroanthracene (Schmidbaur et al., 1990a), (MesSb)ₓ‧C₆H₆ (Ates et al., 1989), SbCl₃‧1,4-bis(2-mercaptoethyl)benzene (Corinne et al., 2009) and a range of tethered diarenes (Burford et al., 1996) with widely differing Sb-ring centroid distances (ca. 2.9–3.8 Å) and arene hapticities (Schmidbaur and Schier, 2008). Furthermore, the π-interaction in η¹-(naphthalene)-(SbCl₃), (Hulme and Szymanski, 1969) has been rationalized as donation of the π electrons of the arene ring into an empty orbital on antimony [originally described as an sp²d² hyrid (Hulme and Szymanski, 1969) but most likely now to be seen as a σ* orbital], resulting in elongation of the Sb-Cl bond trans to the aromatic ring. In general, the interactions between group 15 elements and arenes have been rationalized in terms of a donor-acceptor interaction in which the arene is the donor (Schmidbaur and Schier, 2008). There is no indication among the C-Cl bonds of the C(58)-C(74) ring in 7 [1.380(5)–1.400(5) Å] of a π-arene interaction, although C(53), which sits diametrically opposite Cl(2) [C(53)-C(54) ring is the longest of the three terminal Sb-Cl bonds by ca. 0.1 Å. Furthermore, the point at which antimony makes an orthogonal contact with the C(49)-C(54) ring is displaced 0.471 Å away from the geometric center of the ring in the direction of C(53), from which we surmise that any π-arene...Sb bonding is, at most, η¹ in nature.

The reaction between SbCl₃ and Me₃P proved more difficult to elucidate. SbCl₃, CuCl and Me₃P (1:1:2) were heated to 60°C in toluene and left to cool slowly. Initially, the reaction yielded yellow crystals that were discovered to be twinned, so were redissolved at 100°C and cooled slowly to try to improve their quality. However, on cooling, a yellow precipitate remained with some colorless crystals slowly to try to improve their quality. However, on cooling, a yellow precipitate remained with some colorless crystals on the side of the Schlenk flask which were structurally characterized as [(Me₃P)₂Cu][Sb₂Cl₉] (8), which appears to be a minor hydrolysis product (Figure 8). From a repeat reaction, another minor product was obtained and structurally characterized as [(Me₃P)₂Cu][Sb₂Cl₉] (9) (Figure 9) from a few colorless crystals found within the yellow product. Attempts to discover the nature of the major product in this reaction (the yellow precipitate) failed, as NMR could only confirm the presence of Me₃P groups and microanalysis proved inconclusive.

Figure 8 The asymmetric unit of 8 showing the labeling scheme used. Thermal ellipsoids are at the 40% probability level. Hydrogen atoms, except for those involved in hydrogen bonding, have been omitted for clarity. For selected geometric data, see Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1)-Sb(1)-Cl(2)</td>
<td>89.74(4)</td>
<td>Cl(1)-Sb(1)-Cl(3)</td>
</tr>
<tr>
<td>Cl(1)-Sb(1)-Cl(4)</td>
<td>89.77(3)</td>
<td>Cl(1)-Sb(1)-Cl(5)</td>
</tr>
<tr>
<td>Cl(1)-Sb(1)-Cl(5)</td>
<td>169.86(3)</td>
<td>Cl(2)-Sb(1)-Cl(3)</td>
</tr>
<tr>
<td>Cl(2)-Sb(1)-Cl(4)</td>
<td>87.29(4)</td>
<td>Cl(2)-Sb(1)-Cl(5)</td>
</tr>
<tr>
<td>Cl(2)-Sb(1)-Cl(6)</td>
<td>175.97(4)</td>
<td>Cl(3)-Sb(1)-Cl(4)</td>
</tr>
<tr>
<td>Cl(3)-Sb(1)-Cl(5)</td>
<td>87.24(4)</td>
<td>Cl(3)-Sb(1)-Cl(6)</td>
</tr>
<tr>
<td>Cl(4)-Sb(1)-Cl(5)</td>
<td>174.21(4)</td>
<td>Cl(4)-Sb(1)-Cl(6)</td>
</tr>
<tr>
<td>Cl(5)-Sb(1)-Cl(6)</td>
<td>77.90(3)</td>
<td>Cl(5)-Sb(1)-Cl(7)</td>
</tr>
<tr>
<td>Cl(6)-Sb(1)-Cl(7)</td>
<td>77.90(3)</td>
<td>Cl(6)-Sb(1)-Cl(8)</td>
</tr>
<tr>
<td>Cl(7)-Sb(1)-Cl(8)</td>
<td>77.90(3)</td>
<td>Cl(7)-Sb(1)-Cl(9)</td>
</tr>
<tr>
<td>Cl(8)-Sb(1)-Cl(9)</td>
<td>77.90(3)</td>
<td>Cl(8)-Sb(1)-Cl(10)</td>
</tr>
<tr>
<td>Cl(9)-Sb(1)-Cl(10)</td>
<td>77.90(3)</td>
<td>Cl(9)-Sb(1)-Cl(11)</td>
</tr>
<tr>
<td>Cl(10)-Sb(1)-Cl(11)</td>
<td>77.90(3)</td>
<td>Cl(10)-Sb(1)-Cl(12)</td>
</tr>
<tr>
<td>Cl(11)-Sb(1)-Cl(12)</td>
<td>77.90(3)</td>
<td>Cl(11)-Sb(1)-Cl(13)</td>
</tr>
</tbody>
</table>

Table 1 Selected geometric data (Å, °) for 8.
bimetallic anion is made up from \([\text{Sb}_2\text{Cl}_9]^{3-}\) coordinated to \([\text{Cu}(\text{PPh}_3)_2]^+\) in a \(\kappa^2\)-chelating mode through two chlorine atoms attached to a common antimony \([\text{Sb}(1)]\), each of which bridges dissimilar metals in a \(\mu_2\)-bridging manner. Although a limited number of other examples of \([\text{Sb}_2\text{Cl}_9]^{3-}\) have been structurally characterized (Ishihara et al., 1992; Willey et al., 1996; Wojtas and Jakubas, 2004; Gagor et al., 2008; Fu, 2010; Borisov et al., 2012), this is the first example of it acting as a ligand to coordinate another metal center. In \(8\), copper again adopts a distorted tetrahedral coordination, in which the bond to the bridging \(\text{Cl}(5)\) \([2.3979(11) \, \text{Å}]\) is shorter than that to the hydrogen-bonded \(\text{Cl}(4)\) \([2.5931(12) \, \text{Å}]\); in addition, the \(\text{Cu-PMe}_3\) bonds are the longest noted in this study \([2.2391(12), 2.2337(12) \, \text{Å}]\). The \([\text{Sb}_2\text{Cl}_9]^{3-}\) moiety in \(8\) is considerably distorted in comparison with other examples of this anion as a result of its coordination to copper. The sum of the van der Waals radii for antimony and chlorine (ca. 3.95 Å, given \(\text{Cl} 1.75, \text{Sb} 2.20 \, \text{Å}\)) (Wells, 1984; Emsley, 1991) would allow for three \(\mu_2\)-Cl bridges between the two group 15 elements in \(8\), of which the bridge involving \(\text{Cl}(6)\) is notably longer \([3.6159(12) \, \text{Å}]\) than those involving \(\text{Cl}(3)\) \([3.4951(11) \, \text{Å}]\) or \(\text{Cl}(5)\) \([3.0897(10) \, \text{Å}]\); for comparison, the terminal \(\text{Sb-Cl}\) bonds lie in the range 2.3741(11)–2.5890(11) Å. In contrast, \([\text{Me}_3\text{PH}]^+\) \([\text{Sb}_2\text{Cl}_9]^{3-}\) adopts five phases, the most symmetrical of which has three identical terminal \(\text{Sb-Cl}\) bonds \([2.421(4) \, \text{Å}]\) and three identical bridging interactions \([2.9098(3) \, \text{Å}]\), which become progressively more asymmetric [typically \(\text{Cl}_3\text{Sb} \text{ and } \text{Cl}_3\text{Sb}, \text{ ca. } 2.41–2.54 \text{ and } 2.69–2.85 \, \text{Å}\)] (Gagor et al., 2008), whereas when associated with protonated 1,4,7-trimethyl-1,4,7-triazacyclononane the ranges of \(\text{Sb-Cl}\), \([2.373(4)–2.509(4) \, \text{Å}]\) and \(\text{Sb-Cl}\), \([2.688(5)–3.532(5) \, \text{Å}]\) are more similar to those in \(8\) (Willey et al., 1996). Taking all the above \(\text{Sb-Cl}\) separations in \(8\) as bonds, the two antimony atoms adopt distorted octahedral geometries, with, in each case, one angle more open than expected to accommodate a lone electron pair \([\angle \text{Cl}(1)-\text{Sb}(1)-\text{Cl}(6) 115.48(3); \angle \text{Cl}(3)-\text{Sb}(2)-\text{Cl}(9) 106.96(3)\,\text{°}]\).

Like \(3\), \(9\) contains the common \([\text{Me}_3\text{P}]_4\text{Cu}^+\) cation, which requires no further discussion. Uniquely, however, it also embodies the \([\text{Me}_3\text{P}]_2\text{Sb}_2\text{Cl}_7\)^– anion, for which there is no structural precedent (Figure 9), although the related \([\text{Et}_3\text{PH}]^+\)\([\text{Et}_3\text{P}]_2\text{Sb}_2\text{Br}_7\) has been characterized (Clegg et al., 1994b). The closest structural comparison is with \([\text{Ph}_2\text{Sb}_2\text{Cl}_7]\)^3–, which has a similar arrangement to \(9\) but which incorporates anionic phenyl groups rather than neutral phosphine donors (Sheldrick and Martin, 1992). Compound \(9\) has two anion/cation pairs in the asymmetric unit, and although these are nominally the same as that in \([\text{Ph}_2\text{Sb}_2\text{Cl}_7]\)^3–, that is, the non-halogen substituents are cis to each other with respect to the \(\text{Sb}...\text{Sb}\) vector, all three anions are subtly different. \([\text{Ph}_2\text{Sb}_2\text{Cl}_7]\)^3– is the most regular, having just one \(\mu_2\)-Cl bridge between metals, with two very similar \(\text{Sb-Cl}\) bonds \([\text{ca. } 3.05 \, \text{Å}]\), and terminal \(\text{Sb-Cl}\) \([2.443–2.532 \, \text{Å}](\text{two additional Sb-Cl at ca. } 2.7 \, \text{Å} \text{ are involved in hydrogen bonds to a } [\text{Me}_3\text{NH}]^+ \text{ counterion})\) (Sheldrick and Martin, 1992). In \(9\), the \([\text{Me}_3\text{P}]_2\text{Sb}_2\text{Cl}_7\)^– anion based on \(\text{Sb}(1,2)\) also has only one \(\mu_2\)-Cl bridge, but this is far more substantial \([\text{Sb-Cl}(4) 2.8635(10), 2.8582(12) \, \text{Å}]\); the \(\text{Sb-Cl}\), lie in the range 2.4567(13)–2.6553(11) Å.

Figure 9 One of two \([\text{Me}_3\text{P}]_4\text{Cu}^+\) cations in the asymmetric unit of \(8\) showing the labeling scheme used. Thermal ellipsoids are at the 40% probability level. Hydrogen atoms have been omitted for clarity. For selected geometric data, see Table 2.
Table 2  Selected geometric data (Å, °) for 9.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(1)-Cl(1) 2.4732(12) Sb(3)-Cl(8) 2.5150(12)</td>
<td>Cl(1)-Sb(1)-Cl(6) 89.15(5)</td>
</tr>
<tr>
<td>Sb(1)-Cl(2) 2.5488(13) Sb(3)-Cl(9) 2.6178(13)</td>
<td>Cl(1)-Sb(1)-Cl(7) 112.05(4)</td>
</tr>
<tr>
<td>Sb(1)-Cl(3) 2.6065(13) Sb(3)-Cl(10) 2.5682(13)</td>
<td>Cl(1)-Sb(1)-Cl(8) 101.15(4)</td>
</tr>
<tr>
<td>Sb(1)-Cl(4) 2.8635(10) Sb(3)-Cl(11) 2.7738(11)</td>
<td>Cl(1)-Sb(1)-Cl(9) 109.96(4)</td>
</tr>
<tr>
<td>Sb(1)-Cl(7) 3.7856(14) Sb(3)-Cl(13) 3.5269(12)</td>
<td>Cl(1)-Sb(1)-Cl(10) 115.86(4)</td>
</tr>
<tr>
<td>Sb(2)-Cl(4) 2.8582(12) Sb(4)-Cl(9) 3.6194(14)</td>
<td>Cl(1)-Sb(2)-Cl(5) 109.23(4)</td>
</tr>
<tr>
<td>Sb(2)-Cl(5) 2.4567(13) Sb(4)-Cl(11) 3.0337(11)</td>
<td>Cl(1)-Sb(2)-Cl(6) 116.43(4)</td>
</tr>
<tr>
<td>Sb(2)-Cl(6) 2.6553(11) Sb(4)-Cl(12) 2.4103(13)</td>
<td>Cl(1)-Sb(2)-Cl(7) 116.82(4)</td>
</tr>
<tr>
<td>Sb(2)-Cl(7) 2.5321(11) Sb(4)-Cl(13) 2.5944(12)</td>
<td>Cl(1)-Sb(2)-Cl(8) 116.43(4)</td>
</tr>
<tr>
<td>Sb(1)-P(9) 2.5835(11) Sb(4)-Cl(14) 2.5955(13)</td>
<td>Cl(1)-Sb(2)-Cl(9) 119.72(4)</td>
</tr>
<tr>
<td>Sb(2)-P(10) 2.5807(11) Sb(4)-P(11) 2.5788(12)</td>
<td>Cl(1)-Sb(2)-Cl(10) 124.43(4)</td>
</tr>
</tbody>
</table>

Conclusions

Novel heterobimetallic M-Cl-M′ adducts (M, M′=Cu, Zn, Sn, Sb) have been prepared and structurally characterized. We have had no success in isolating clean products from the further nucleophilic substitution of Cl with, for example, SR, to generate M-S(R)-M′ precursors for CVD, which suggests that under the reaction conditions employed the adducts fragment. However, this work has shown that M-X-M′ can be made, and we have had more success in generating such M-S(R)-M′ species by direct assembly from, for example, [Zn(SR)2] and (R,P)CuCl, details of which will form part of a separate report.

Experimental section

General procedures

All operations were performed under an atmosphere of dry argon using standard Schlenk line and glove box techniques. Toluene was dried using a commercially available solvent purification system (Innovative Technology Inc., MA, USA) and degassed under argon prior to use. Tetrahydrofuran (THF) was dried by refluxing over potassium before isolating by distillation and degassing under argon prior to use. Deuterated benzene (C6D6) and deuterated chloroform (CDCl3) NMR solvents were purchased from Fluorochem (Hadfield, UK), and dried by refluxing over potassium and over 4 Å molecular sieves respectively, before isolating via vacuum distillation. All dry solvents were stored under argon in Young’s ampoules over 4 Å molecular sieves.

Melting points were determined utilizing a Stuart SMP10 Melting Point Apparatus (Bibby Scientific Ltd, Stone, UK). Elemental analyses were performed externally by London Metropolitan University Elemental Analysis Service, UK. Solution 1H, 13C{1H}, 31P{1H} and 119Sn{1H} NMR spectra were recorded with a Bruker Avance 300...
spectrum (Bruker, Coventry, UK) at ambient temperature (25°C), save for the 119Sn{1H} NMR spectrum of 5, which was recorded at 233 K on a Bruker Avance 400 spectrometer. 1H and 13C NMR chemical shifts are referenced internally to residual non-deuterated solvent resonances. All chemical shifts are reported in δ (ppm) and coupling constants in hertz. The following abbreviations are used: d (doublet), m (multiplet) and br (broad).

Synthesis of [(Ph3P)2CuCl]2-ZnCl2 (1): (Ph3P)2CuCl (1.00 g, 1.61 mmol) and ZnCl2 (0.11 g, 0.80 mmol) were stirred together in toluene (50 mL) at 80°C for 4 h. After 4 h, all solids had dissolved. White crystals were obtained on slow cooling of the solution to room temperature (0.97 g, 92%, mp 242–244°C). Analysis, found (calc. for C6H18P2Cl4CuZn): C 14.9 (15.0), H 3.62 (3.77). 1H NMR (300 MHz, CD2Cl2) δ (ppm): -2.4. 13C NMR (300 MHz, CD2Cl2) δ (ppm): 15.4 (d, J=18.0 Hz, Me), 13P NMR (300 MHz, CD2Cl2) δ (ppm): -45.3.

Also prepared using the same method was (Me3P)2CuCl2-ZnCl2 (8): Using Me3P (1 g, 13.14 mmol), CuCl (0.64 g, 6.58 mmol) and SnCl2 (1.48 g, 6.58 mmol) were heated in toluene at 60°C for 1 h. Redissolving the yellow precipitate formed by heating to 100°C and leaving to cool slowly to room temperature produced a few colorless crystals, enough for X-ray crystallography, but no further analysis was carried out.

Also prepared using the same method was [(Me3P)CuCl]2-ZnCl2 (9): Using Me3P (1 g, 13.14 mmol), CuCl (0.64 g, 6.58 mmol) and SnCl2 (1.48 g, 6.58 mmol). A few crystals suitable for diffraction were obtained by heating the solution to 100°C and cooling slowly in an oil bath, but no further analysis was carried out.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarized in Table 3. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-Kα radiation (λ=0.71073 Å). Structure solution followed by full-matrix least squares refinement was performed using the WinGX-L70 suite of programs (Farrugia, 1999). Corrections for absorption (multiscan) were made in all cases.

Specific details: 1: The asymmetric unit consists of half a complete molecular entity, the remainder generated by a crystallographic twofold axis coincident with the zinc center. Additionally, there are four toluene entities present, two of which [C(41)-C(47), C(51)-C(57)] straddle crystallographic twofold rotation axes and are hence disordered about some. The third region of solvent presents as half a molecular entity, the remainder generated by a crystallographic twofold rotation axis and is hence disordered about some. The third region of solvent presents as half a molecular entity, [C(71)-C(77)], which is proximate to an inversion center. This necessarily means that the methyl group position is disordered over two places on the phenyl ring. This solvent fragment is further disordered with a proximate half-occupancy toluene [C(61)-C(67)]. The level of disorder in this latter region of the electron density map necessitated the inclusion of some geometric restraints in order to assist convergence. 4: Contains a molecule of lattice toluene. 5: Satisfactory structure determination and refinement could only be brokered once pseudo-merohedral twinning (36%, about the 100 direct lattice direction) had been accounted for and the data were analyzed in space group P1 with four independent molecules in the asymmetric unit; ADP restraints were applied to three carbon atoms to assist convergence and some B alerts remain in the final cifcheck. The composition of the final product has, however, been unambiguously determined. 7: The asymmetric unit includes 1.5 molecules of toluene. The toluene based on C(61)-C(67) is disordered close to a center of inversion and therefore has an occupation factor of 50%; toluene C(71)-C(77) is disordered in the ratio 1:1 and was isotropically refined, with a restraint applied to the C(71)-C(77) distance. All solvent C6 rings were constrained to being ideal hexagons. 9: The Me3P moiety based on P(4) was seen to be disordered in a 70:30 ratio. P-C distances therein were refined subject to being similar, and some
| Chemical formula | Formula mass | Crystal system | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) | Unit cell volume (Å³) | Space group | Z | μ (Mo-kα) (mm⁻¹) | Reflections measured | Independent reflections | Final R₁ values [I>2σ(I)] | Final wR(F) values [I>2σ(I)] | Final R₁ values (all data) | Final wR(F) values (all data) | Goodness of fit on F² | Flack parameter | Largest diff. peak and hole (eÅ⁻³) |
|------------------|--------------|----------------|-------|-------|-------|-------|-------|-------|----------------------|--------------|----|------------------|------------------------|--------------------------|---------------------------|-----------------------------|-----------------------------|----------------------------|-----------------|-------------------------------|
| C₁₉₃H₁₇₅Cl₈Cu₄P₈Zn₂ | 3410.59      | Monoclinic     | 21.7997(4) | 8.9728(2) | 15.1682(2) | 89.0275(14) | 102.863(1) | 87.3021(13) | 1866.26(7) | C2/c | 2 | 0.1032 | 72180                  | 9600                   | 0.0521                   | 0.0714                      | 0.0552                      | 0.0796                       | 1.013                   | -0.009(14) | -0.613, -0.897 |
| C₆H₁₈Cl₄Cu₂P₂Zn | 486.39       | Monoclinic     | 8.9728(2) | 11.4549(3) | 19.7345(4) | 19.8414(2) | 14.1197(2) | 3971.17(10) | 1697.11(7) | P2₁/n | 4 | 0.0619 | 4674                  | 72180                  | 0.0619                   | 0.0716                      | 0.0452                      | 0.0772                       | 1.073                   | 0.320, -0.319 | 0.427, -0.597 |
| C₁₈H₅₄Cl₄Cu₂P₆Zn | 790.68       | Triclinic      | 9.6824(2) | 9.8414(2) | 19.7345(4) | 19.8414(2) | 14.1197(2) | 3971.17(10) | 1697.11(7) | P1   | 2 | 0.0500 | 2318                  | 29776                  | 0.0500                   | 0.0726                      | 0.0547                      | 0.0795                       | 1.073                   | 0.613, -0.897 | 0.427, -0.597 |
| C₄₃H₃₈Cl₃CuP₂Sn | 905.25       | Orthorhombic   | 9.5878(1) | 14.1197(2) | 29.3342(5) | 15.2860(6) | 14.7604(6) | 12453.78(12) | 2504.20       | P2₁/2₁₂₁ | 24 | 0.0844 | 0.613                  | 26811                 | 0.0844                   | 0.0762                      | 0.0581                      | 0.0844                       | 1.073                   | -0.009(14) | -0.613, -0.897 |
| C₉H₂₇Cl₃CuP₃Sn | 516.80       | Triclinic      | 9.6870(4) | 15.2860(6) | 15.3330(4) | 15.2860(6) | 14.7604(6) | 12453.78(12) | 2504.20       | P1   | 2 | 0.0861 | 0.1477                  | 42219                 | 0.0861                   | 0.0335                      | 0.0581                      | 0.0844                       | 1.073                   | 0.320, -0.319 | 0.427, -0.597 |
| C₃₆H₃₀Cl₄CuP₂Sb | 851.63       | Monoclinic     | 10.9622(4) | 11.1033(4) | 101.575(2) | 101.575(2) | 95.532(1)  | 1743.96(11) | 1697.11(7) | P2₁/2₁₂₁ | 2 | 0.1032 | 2.318                 | 26811                 | 0.1477                   | 0.0335                      | 0.0581                      | 0.0844                       | 1.073                   | 0.613, -0.897 | 0.427, -0.597 |
| C₁₂₉H₁₁₄Cl₈Cu₂P₆Sb₂ | 2504.20      | Orthorhombic   | 12.8356(1) | 11.033(4) | 101.575(2) | 101.575(2) | 95.532(1)  | 1743.96(11) | 1697.11(7) | P2₁/2₁₂₁ | 2 | 0.1064 | 1.477                  | 42219                 | 0.1477                   | 0.0335                      | 0.0581                      | 0.0844                       | 1.073                   | 0.613, -0.897 | 0.427, -0.597 |
| C₁₂H₃₈Cl₉CuP₄Sb₂ | 932.39       | Monoclinic     | 14.9358(1) | 11.1033(4) | 101.575(2) | 101.575(2) | 95.532(1)  | 1743.96(11) | 1697.11(7) | P2₁/2₁₂₁ | 2 | 0.1064 | 1.477                  | 42219                 | 0.1477                   | 0.0335                      | 0.0581                      | 0.0844                       | 1.073                   | 0.613, -0.897 | 0.427, -0.597 |
| C₃₆H₁₀₈Cl₁₄Cu₂P₁₂Sb₄ | 2023.24      | Monoclinic     | 14.9358(1) | 11.1033(4) | 101.575(2) | 101.575(2) | 95.532(1)  | 1743.96(11) | 1697.11(7) | P2₁/2₁₂₁ | 2 | 0.1064 | 1.477                  | 42219                 | 0.1477                   | 0.0335                      | 0.0581                      | 0.0844                       | 1.073                   | 0.613, -0.897 | 0.427, -0.597 |
ADP restraints were added to the fractional occupancy carbons to assist convergence.

Supporting information

Crystallographic data for the structural analysis (in CIF format) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 970317–970325 for 1–9, respectively. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgments: We thank the EPSRC for financial support through the PV21 Supergen program, and Stephen Boyer, London Metropolitan University, UK, for performing the microanalyses.

Received November 18, 2013; accepted January 20, 2014; previously published online March 10, 2014

References


Schmidbaur, H.; Nowak, R.; Huber, B.; Mueller, G. Hexaethynylbenzene-trichloroantimony: a Menshutkin complex with a \(\eta^6\)-aryl)


Sheldrick, W. S.; Martin, C. Preparation and crystal-structures of chlorophenylantimonates(III) and bromophenylantimonates(III) \([\text{Ph}_2\text{SbX}]_n\) \([\text{X}=(\text{Cl}, \text{Br})]\). \textit{Z. Naturforsch., B: Chem. Sci.} 1992, \textit{47}, 919–924.


Willey, G. R.; Daly, L. T.; Meehan, P. R.; Drew, M. G. B. Controlled hydrolysis reactions of the group 15 element-azaamacyclooctane complexes MCl\(_4\) (M=As, Sb or Bi; L=1,4,7-trizacyclo-1,4,7-triazacyclooctane). Formation and crystal structures of \([\text{AsCl}_4]\)\([\text{AsCl}_4]\), \([\text{H}_2]\)\([\text{SbCl}_4]\), \([\text{HL}]\)\([\text{H}_2]\)\([\text{SbCl}_4]\), \([\text{H}_3]\)\([\text{SbCl}_4]\) and \([\text{H}_4]\)\([\text{SbCl}_4]\) \text{Cl-MeCN-H.O. J. Chem. Soc., Dalton Trans.} 1996, \textit{26}, 4045–4053.

