

# Preparation and structures of the mixed-metal clusters Pt<sub>2</sub>M<sub>2</sub>Se<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> (M = Cu, Ag) and Pd<sub>2</sub>Au<sub>2</sub>Se<sub>2</sub>(SeH)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>. An entry to ternary clusters

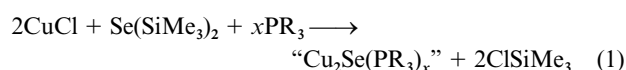
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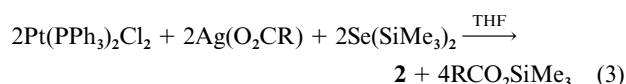
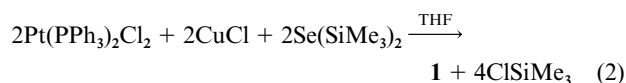
Both *cis*- and *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> react with Se(SiMe<sub>3</sub>)<sub>2</sub> and CuCl or AgO<sub>2</sub>CR (R = Me, Ph) in THF to form the mixed-metal clusters Pt<sub>2</sub>M<sub>2</sub>Se<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> (M = Cu or Ag, respectively), and likewise Au(PPh<sub>3</sub>)Cl reacts with Pd(acac)<sub>2</sub>, to form Pd<sub>2</sub>Au<sub>2</sub>Se<sub>2</sub>(SeH)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>.

The preparation of copper chalcogenide clusters is of great interest for the synthesis of nanoparticles.<sup>1</sup> The preparation of the largest crystallographically characterized copper cluster, Cu<sub>146</sub>Se<sub>73</sub>(PPh<sub>3</sub>)<sub>30</sub>, was recently reported, along with a number of other clusters with different nuclearities.<sup>1</sup> The synthesis of such materials follows this general reaction scheme:

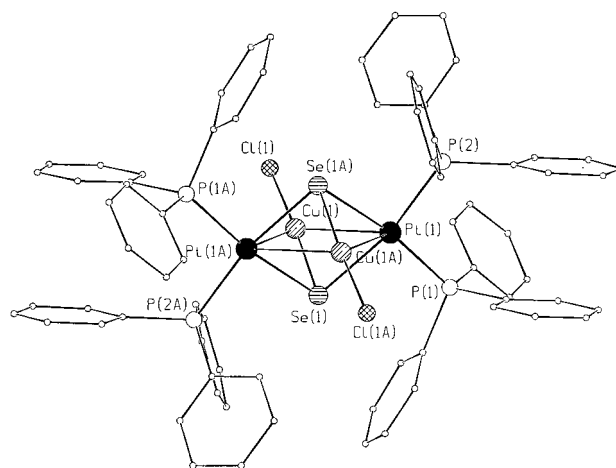


where PR<sub>3</sub> is either an alkyl, aryl or mixed alkyl/aryl phosphine. This chemistry has also been extended to silver, and similar results have been obtained.<sup>1</sup> Binary systems of the type Pt/Se, Pt/Te and Au/Se have been explored by various groups, and the preparations of binuclear and trinuclear species such as (PPh<sub>3</sub>)<sub>2</sub>-Pt(μ-Se)<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub>,<sup>2</sup> L<sub>2</sub>Pt(μ-Te)<sub>2</sub>PtL<sub>2</sub> (L = PPh<sub>3</sub>, PET<sub>3</sub>; L<sub>2</sub> = dpmp),<sup>3</sup> Pt<sub>3</sub>Se<sub>2</sub>(dppe)<sub>3</sub>,<sup>3</sup> [Se(AuPPh<sub>3</sub>)<sub>3</sub>]PF<sub>6</sub> and Au<sub>2</sub>Se(PPh<sub>3</sub>)<sub>2</sub>,<sup>4</sup> have also been reported. In this work we wish to take advantage of the capacity of the Se atom to coordinate an extra M group in order to promote M–M' bonding, and mixed-metal cluster formation. The synthesis and crystal structures of three novel ternary clusters, Pt<sub>2</sub>M<sub>2</sub>Se<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> (M = Cu **1**, Ag **2**), and Pd<sub>2</sub>Au<sub>2</sub>Se<sub>2</sub>(SeH)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> **3** which are the first examples of cluster compounds containing Pt/Cu/Se, Pt/Ag/Se,<sup>‡</sup> and Pd/Au/Se are now presented. These compounds represent potential precursors as an entry to larger mixed-metal clusters *via* the presence of displaceable Cl atoms, and phosphine groups. In relation with this study, we find that examples of Pt–Cu bond-containing clusters are rather rare, where only six have been characterized from X-ray crystallography.<sup>5</sup> For the Pt–Ag analogues, many more examples are known.<sup>6</sup>

The clusters **1** and **2** can easily be prepared from the following general reactions:<sup>§</sup>



where R = Me, or Ph, and the Pt(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> species can be either the *cis*- or *trans*-isomers. When the chalcogenide reagent Se(SiMe<sub>3</sub>)<sub>2</sub> is slowly added dropwise into solutions containing Pt(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and CuCl or AgO<sub>2</sub>CR (R = Me, Ph) in stoichiometric amount (1 : 1 : 1) in the presence of 2 equivalents of PPh<sub>3</sub>, and at –40 °C, the solutions pass from a deep yellow to a dark brown coloration. Upon slowly warming the solutions to room temperature over several hours, and letting them sit for several days, large orange crystals were readily obtained, and were

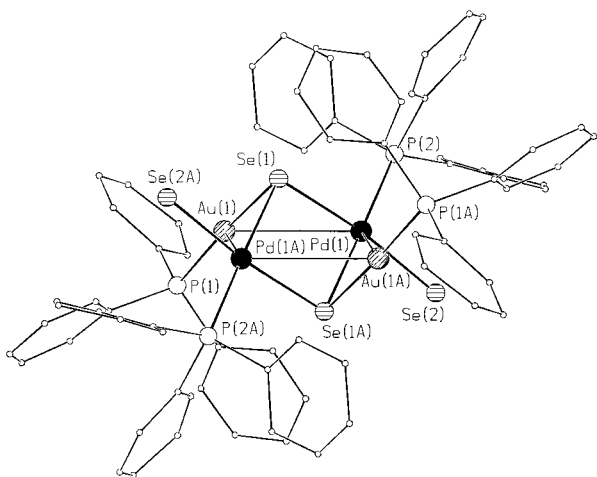


**Fig. 1** Molecular structure for clusters **1** and **2**. The H-atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows; **1**: Pt–Se 2.474(1), 2.485(1), Pt–P 2.279(2), 2.291(2), Pt–Cu 2.916(1), 3.047(1), Cu–Cl 2.129(3), Cu–Se 2.274(1), Se...Se 3.254(2), Pt...Pt 3.753(2); Se–Pt–Se 82.04(3), P–Pt–P 100.30(7), Pt–Se–Pt 97.96(3), Se–Cu–Cl 176.90(11)°. **2**: Pt–Se 2.509(2), 2.478(1), Pt–P 2.293(4), 2.318(3), Pt–Ag 3.028(2), 3.037(1), Ag–Cl 2.361(5), Ag–Se 2.548(2), Se...Se 3.253(3), Pt...Pt 3.781(3); Se–Pt–Se 81.42(5), P–Pt–P 96.63(12), Pt–Se–Pt 98.58(5), Se–Ag–Cl 171.59(15)°.

identified from X-ray crystallography as Pt<sub>2</sub>M<sub>2</sub>Se<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> (M = Cu, Ag).

The X-ray structure analysis<sup>¶</sup> reveal the isostructural behavior of these two isocentric clusters, where two M–Cl units sit above and under the planar P<sub>2</sub>Pt(μ-Se)<sub>2</sub>PtP<sub>2</sub> fragment, and the Pt<sub>2</sub>M<sub>2</sub>Se<sub>2</sub> core forms a strongly distorted octahedral structure (C<sub>2h</sub> symmetry, see Fig. 1). The coordination of the M–Cl units occurs *via* only one formal Se–M single bond with distances [*d*(Se–Cu) 2.274(1), *d*(Se–Ag) 2.548(2) Å] that are normal in comparison with the related binary “M<sub>2</sub>Se(PR<sub>3</sub>)<sub>x</sub>” clusters (M = Cu, Ag).<sup>1</sup> Thus the Se atoms adopt a μ<sub>3</sub>-binding mode with Pt–Se bond distances of 2.474(1) and 2.485(1) Å for M = Cu, and 2.509(2) and 2.478(1) Å for M = Ag. The Pt–Se–Pt and Pt–Se–M angles are 97.96(3), and 79.70(4) and 74.44(4)° for M = Cu, and 98.58(5), and 74.32(5) and 73.56(6)°, for M = Ag. The smaller Pt–Se–M angles are associated with the presence of Pt...M interactions. Indeed no formal Pt–M bonding occurs where the Pt–M distances range from ≈2.92 to 3.05 Å. This result contrasts greatly with all Pt–Cu bond-containing clusters for which the Pt–Cu bonds are reported to be ≈2.53 < *d*(Pt–Cu) < ≈2.74 Å.<sup>5</sup> Despite the long Pt–Cu distance, significant Pt...Cu interactions are readily anticipated,<sup>7</sup> as these values are located well inside the sum of the van der Waals radii. On the other hand for the Pt<sub>2</sub>Ag<sub>2</sub> analogue, such distances are not uncommon in the literature.<sup>6</sup> Such interactions are also felt in the Se–M–Cl angles which deviate slightly from linearity generally encountered in pure sp hybridation.

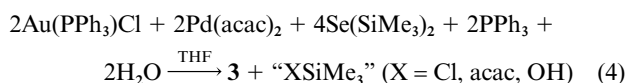
The “(PPh<sub>3</sub>)<sub>2</sub>Pt(μ-Se)<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub>” frame is not greatly affected



**Fig. 2** Molecular structure for **3**. The H-atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Au–Se 2.412(2), Au–P 2.261(6), Au–Pd 3.067(2), 3.300(2), Pd–Se(H) 2.446(3) Pd–Se 2.486(3); Se–Au–P 176.4(1), Se–Pd–P 175.5(2), Se–Pd–Se 84.8(1), P–Pd–Se(H) 93.2(2), Pd–Se–Pd 95.2(1)°.

upon complexation with the M–Cl groups. However, by comparison with the literature data reported for the “free”  $(\text{PPh}_3)_2\text{Pt}(\mu\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$  dimer,<sup>2</sup> some bond distances have increased. Indeed the average Pt–Se and Pt–P bond lengths are 2.449 and 2.277 Å for  $\text{Pt}_2\text{Se}_2(\text{Ph}_3)_4$ ,<sup>2</sup> 2.480 and 2.285 Å for **1**, and 2.494 and 2.306 Å for **2**, respectively. This effect is clearly steric on one side, but also some electronic factors such as electronic density change at the Pt atoms promoting  $\text{Pt} \cdots \text{M}$  interactions, could also contribute to the bond length variations.

Cluster **3** can be prepared in a similar fashion in the dark in reasonable yield according to:



**3** crystallizes as red-orange crystals. This time the excess of  $\text{PPh}_3$  is not used as a stabilizing/solubilizing agent, but as a reactant. X-Ray crystallographic analysis indicates that **3** is also a centrosymmetric cluster (point group  $C_i$ ), again showing a strongly distorted  $\text{Pd}_2\text{Au}_2\text{Se}_2$  octahedral (Fig. 2). As for **1** and **2**, the  $d^{10}$  electronic configuration metal is bonded to the  $d^8$ – $d^8$  dimer  $(\text{PPh}_3)(\text{SeH})\text{Pd}(\mu\text{-Se})_2\text{Pd}(\text{PPh}_3)(\text{SeH})$  ( $C_{2h}$  point group) *via* a formal Se–Au single bond [2.412(2) Å] leading to weak  $\text{Pd}^{\text{II}} \cdots \text{Au}^{\text{I}}$  contacts [3.067(2) and 3.300(2) Å].<sup>7</sup> Both Pd and Au carry a single  $\text{PPh}_3$  ligand which differs from **1** and **2** where both  $\text{PPh}_3$ 's are bonded to the Pt only. One other difference is the presence of SeH groups [<sup>1</sup>H NMR  $\delta$ (ppm) 0.123] instead of Cl.

The fact that clusters **1** and **2** have extra Cl atoms and **3** exhibits SeH centers opens the door to further extension of this chemistry towards larger clusters or the incorporation or another type of metal. Further research in this area is in progress.

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## Notes and references

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‡ According to the Cambridge Data Bank a compound formulated as

$[(\text{PPh}_3)_2\text{PtAg}_2\text{SeCo}\{(\text{PPh}_2\text{CH}_2\text{CH}_2)_3\text{CMe}\}]\text{BF}_4$  has been described in G. Baldi, M. di Vaira, L. Niccolai, M. Peruzzini and P. Stoppioni, *Eur. Cryst. Meeting*, 1985, **9**, 164, but no formal report of this cluster exists.

§ Preparation of **1**: 0.35 g (0.50 mmol) of either *cis*- or *trans*- $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$  was mixed with 0.050 g (0.50 mmol) of dry  $\text{CuCl}$  and 0.26 g (1.0 mmol) of  $\text{PPh}_3$  in 20 ml of dry THF under  $\text{N}_2(\text{g})$  at room temperature. Then the unstirred solution was cooled to  $\approx -40^\circ\text{C}$  using an acetone bath and  $\text{N}_2(\text{l})$ , prior to slow addition of  $\approx 0.10$  ml (1.1 mmol) of  $\text{Se}(\text{SiMe}_3)_2$ . The solution turned yellow, pale orange, and deep brown during these additions. The solution was then allowed to warm up over several hours until room temperature was reached. After several days in the dark, large orange crystals readily appeared and were collected for X-ray analysis. Yield  $\approx 50\%$ . <sup>31</sup>P NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  28.23 [<sup>1</sup> $J(\text{P}_a\text{Pt}) = 3057$ , <sup>1</sup> $J(\text{P}_b\text{Pt}) = 2964$ ; <sup>3</sup> $J(\text{P}_a\text{Pt}) = 1564$ , <sup>3</sup> $J(\text{P}_b\text{Pt}) = 1442$ ; <sup>2</sup> $J(\text{PP}) = 88\text{Hz}$ ]. Preparation of **2**: this cluster was prepared in the same way as described for **1** except that both  $\text{AgO}_2\text{CR}$  starting materials ( $\text{R} = \text{Me, Ph}$ ) were used (0.085 g, 0.50 mmol,  $\text{R} = \text{Me}$ ; 0.11 g, 0.50 mmol,  $\text{R} = \text{Ph}$ ), instead of  $\text{CuCl}$  and the solution was kept in the dark at all times. Orange crystals were obtained in all cases over a period of several weeks. For the crystal reported in this work, an addition of a wet acetone (unpurified)–benzene mixture to the THF solutions was used. Crystallisation appeared more rapidly ( $\approx 1$  day). Yield  $\approx 80\%$ . <sup>31</sup>P NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  27.94 [<sup>1</sup> $J(\text{P}_a\text{Pt}) = 2984$ , <sup>1</sup> $J(\text{P}_b\text{Pt}) = 2882$ ; <sup>3</sup> $J(\text{P}_a\text{Pt}) = 1615$ , <sup>3</sup> $J(\text{P}_b\text{Pt}) = 1426$ ; <sup>2</sup> $J(\text{PP}) = 92\text{Hz}$ ]. Preparation of **3**: 0.30 g (1 mmol) of  $\text{Pd}(\text{acac})_2$ , 0.49 g (1 mmol) of  $\text{Au}(\text{PPh}_3)\text{Cl}$  and 0.52 g (2 mmol) of  $\text{PPh}_3$  (excess) were dissolved in 25 ml of THF at room temperature. Then the solution was cooled to  $\approx -40^\circ\text{C}$  and kept in the dark prior to adding 0.50 ml ( $\approx 3$  mmol) of  $\text{Se}(\text{SiMe}_3)_2$ . The solution was allowed to warm to room temperature over several hours. After several days in the dark, water was introduced very slowly into the solution over a period of several days and orange-red crystals appeared over this addition period. The crystals are light stable. Yield  $\approx 50\%$ . <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.123 and 0.300 [SeH, <sup>1</sup> $J(\text{SeH}) = 3.3\text{Hz}$ ] for compounds **a** and **b** (chemical exchange in solution), 6.8–7.5 ( $\text{C}_6\text{H}_5\text{P}$ , br bands). <sup>31</sup>P NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  6.6 (free  $\text{PPh}_3$  in chemical exchange, very br), 16–30 (PdP and AuP, complex, both isomers).

¶ Crystal data. For **1**·THF:  $\text{C}_{80}\text{H}_{60}\text{Cl}_2\text{Cu}_2\text{O}_2\text{P}_4\text{Pt}_2\text{Se}_2$ , orange plate,  $M = 961.62$ , monoclinic, space group  $P2_1/n$ ,  $a = 14.828(3)$ ,  $b = 14.221(3)$ ,  $c = 18.032(4)$  Å,  $\beta = 102.62(3)^\circ$ ,  $V = 3710.5(13)$  Å<sup>3</sup>, at 200(2) K,  $Z = 2$ ,  $D_c = 1.721\text{g cm}^{-3}$ ,  $\mu = 5.509\text{mm}^{-1}$ ,  $2\theta_{\text{max}} = 52.02^\circ$ , 7117 independent reflections measured ( $R_{\text{int}} = 0.1104$ ) on a STOE IPDS diffractometer. All Pt, Cu, Se, Cl and C atoms were refined anisotropically, to yield  $R = 0.0632$ ,  $wR_2 = 0.1696$ ,  $S = 1.013$  for 6365 data [ $F_o > 4\sigma F_o$ ]. For **2**· $\text{C}_6\text{H}_6$ · $2\text{H}_2\text{O}$ :  $\text{C}_{78}\text{H}_{60}\text{Ag}_2\text{Cl}_2\text{O}_2\text{P}_4\text{Pt}_2\text{Se}_2$ , small orange hexagonal plate,  $M = 1987.88$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.386(2)$ ,  $b = 13.499(3)$ ,  $c = 14.169(3)$  Å,  $\alpha = 64.73(3)^\circ$ ,  $\beta = 80.95(3)^\circ$ ,  $\gamma = 70.48(3)^\circ$ ,  $V = 1854.7(6)$  Å<sup>3</sup>, at 200(2) K,  $Z = 1$ ,  $D_c = 1.780\text{g cm}^{-3}$ ,  $\mu = 5.464\text{mm}^{-1}$ ,  $2\theta_{\text{max}} = 52.08^\circ$ , 5205 independent reflections measured ( $R_{\text{int}} = 0.0529$ ) on a STOE IPDS diffractometer. All C, Ag, Cl, O, P, Pt and Se atoms were refined anisotropically to yield  $R = 0.0651$ ,  $wR_2 = 0.1850$ ,  $S = 1.117$  for 4434 [ $F_o > 4\sigma F_o$ ]. For **3**· $2\text{THF}$ :  $\text{C}_{80}\text{H}_{76}\text{Au}_2\text{O}_2\text{P}_4\text{Pd}_2\text{Se}_4$ , orange-red plate fragment,  $M = 2099.73$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.004(2)$ ,  $b = 12.939(3)$ ,  $c = 14.452(3)$  Å,  $\alpha = 70.27(3)^\circ$ ,  $\beta = 76.32(3)^\circ$ ,  $\gamma = 82.27(3)^\circ$ ,  $V = 1878.6(7)$  Å<sup>3</sup>, at 200(2) K,  $Z = 1$ ,  $D_c = 1.856\text{g cm}^{-3}$ ,  $\mu = 6.432\text{mm}^{-1}$ ,  $2\theta_{\text{max}} = 45.00^\circ$ , 3693 independent reflections measured ( $R_{\text{int}} = 0.0732$ ) on a STOE IPDS diffractometer. All C, Au, O, P, Pd, and Se atoms were refined anisotropically, to yield  $R = 0.0747$ ,  $wR_2 = 0.1826$ ,  $S = 1.011$  for 2657 data [ $F_o > 4\sigma F_o$ ]. CCDC reference number 186/1205. See <http://www.rsc.org/suppdata/dt/1998/3901/> for crystallographic files in .cif format.

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