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Non-bonded *vs.* Bonded Interactions in $(Ph_3P)_4Ag_2Br_2$–$(Ph_3P)_4Ag_4Br_4$ and its Stereochemical Analogue $[(RS)_4Fe_2S_2]^{2-}$–$[(RS)_4Fe_4S_4]^{2-}$

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Summary The stereochemistry of the metal–metal non-bonded dimer–tetramer pair $(Ph_3P)_4Ag_2Br_2$–$(Ph_3P)_4Ag_4Br_4$ exhibits trends resembling those of the structurally analogous metal–metal bonded pair $[(RS)_4Fe_2S_2]^{2-}$–$[(RS)_4Fe_4S_4]^{2-}$, indicating that the metal atoms within each pair probably bear similar gross atomic charges.

We report here the stereochemistries of a new silver dimer $(Ph_3P)_4Ag_2Br_2$ (**1**) and the corresponding tetramer $(Ph_3P)_4Ag_4Br_4$ (**2**). The dimer (**1**) has a hitherto unreported dimeric structure in the solid state (for the phosphine–silver halide cluster family), in contrast to the monomeric formulation of $[(C_7H_7)_3P]_2AgBr$[1] in solution. The geometrical characteristics of (**1**) provide a rationale for the ease of formation of $(Ph_3P)_3Cu_2Cl_2$[2] with respect to the yet unknown $(Ph_3P)_4Cu_2Cl_2$. The tetramer (**2**) possesses a distorted cubane-like structure. A detailed comparison of (**1**) and (**2**) shows the influence of steric *vs.* electronic effects on their stereochemistries in going from a dimer to a tetramer. This relationship is also compared with that observed in the metal–metal bonded $[(RS)_4Fe_2S_2]^{2-}$–$[(RS)_4Fe_4S_4]^{2-}$ pair.[3]

The dimer $(Ph_3P)_4Ag_2Br_2$ (**1**) was prepared by refluxing a stoicheiometric amount of triphenylphosphine with silver bromide in acetonitrile, whereas the tetramer $(Ph_3P)_4Ag_4Br_4$ (**2**) was prepared as previously described.[4] Slow crystallization of (**1**) and (**2**) from $CHCl_3$–Et_2O afforded rod- and rhombohedral-shaped colourless crystals, respectively. *X*-Ray structural determinations have shown that (**1**) is a dimer with two equivalent $(Ph_3P)_2Ag$ groupings bridged by two bromine atoms (Figure 1)† whereas (**2**) is a tetramer with a cubane-like structure (Figure 2).‡ The silver atoms in both (**1**) and (**2**) are approximately tetrahedral.

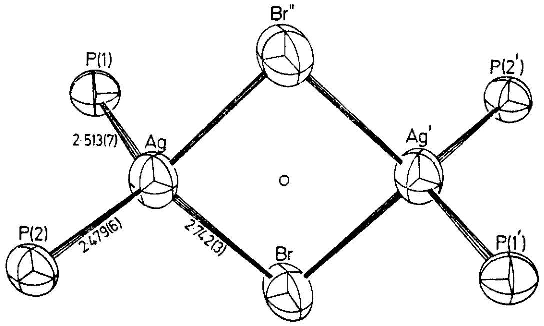

FIGURE 1. The $P_4Ag_2Br_2$ core of $(Ph_3P)_4Ag_2Br_2$; Ag · · · Ag′ 3·720 (4) and Br · · · Br″ 4·030(6) Å.

The $P_4Ag_2Br_2$ core of the dimer (**1**) has a crystallographic site symmetry of $C_{2h} - 2/m$. It is degraded from D_{2h} symmetry by a twist of 6·4° of the two P_2Ag groupings (in the opposite sense) along the direction of the two bridging

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† $(Ph_3P)_4Ag_2Br_2{\cdot}CHCl_3$ (**1**): monoclinic, $I2/m$, $a = 14{\cdot}311$ (2), $b = 17{\cdot}624$ (3), $c = 14{\cdot}961$ (3) Å; $\beta = 96{\cdot}56$ (1)°, $Z = 2$. Anisotropic–isotropic least-squares refinement gave $R_1 = 8{\cdot}04$ and $R_2 = 13{\cdot}64\%$ for 1526 independent reflections.

‡ $(Ph_3P)_4Ag_4Br_4$ (**2**): rhombohedral, $R3c$, $a = 17{\cdot}494(5)$ Å, $\alpha = 56{\cdot}01$ (2)°, $Z = 2$. Anisotropic least-squares refinement gave $R_1 = 2{\cdot}80$ and $R_2 = 3{\cdot}17\%$ for 1613 independent reflections.

bromine atoms. This effect can be attributed to intramolecular nonbonding repulsions involving the phenyl groups and the bromine atoms shown by a wide range of close (Ph)H ··· H(Ph) and (Ph)H ··· Br contacts. We believe that this ligand overcrowding, which manifests itself in unequal Ag–P distances and P–Ag–Br angles, should be substantially enhanced when the silver atoms are replaced by much smaller copper atoms, thereby rendering $(Ph_3P)_4Cu_2X_2$ sterically unfavourable with respect to $(Ph_3P)_3Cu_2X_2$.[2] This may explain why compounds of the type $(Ph_3P)_4Cu_2X_2$ are relatively rare for $X^- =$ halide but common for $X^- = N_3^-$,[5] and NCS^-.[6]

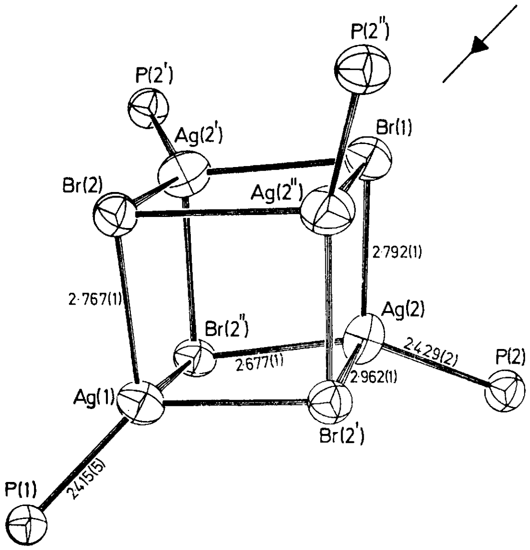

FIGURE 2. The $P_4Ag_4Br_4$ core of $(Ph_3P)_4Ag_4Br_4$; Ag(1) ··· Ag(2) 3·930(1), Ag(2) ··· Ag(2′) 3·719(2), Br(1) ··· Br(2) 4·200(1), and Br(2) ··· Br(2′) 3·964(2) Å.

The $P_4Ag_4Br_4$ core of the tetramer (**2**) conforms to a crystallographic $C_3 - 3$ site symmetry. Its departure from C_{3v} symmetry is shown by nonequal Ag(2)–Br(2) distances and P(2)–Ag(2)–Br(2) angles. The intermediate C_{3v} symmetry is degraded from the idealized T_d symmetry by an elongation along the threefold axis (body diagonal Ag(1) ··· Br(1)) which results in three long Ag(1) ··· Ag(2) and Br(1) ··· Br(2) distances and three short Ag(2) ··· Ag(2′) and Br(2) ··· Br(2′) distances (Figure 2). Again, this significant distortion can be attributed to intramolecular nonbonding repulsions of the types (Ph)H ··· H(Ph) and (Ph)H ··· Br.

The significance of this dimer (**1**)–tetramer (**2**) pair lies in the comparison of their stereochemistry with the iron–sulphur protein model $[(RS)_4Fe_2S_2]^{2-}$ (**3**)–$[(RS)_4Fe_4S_4]^{2-}$ (**4**). Despite the dimensional differences [*viz.*, nonbonding Ag ··· Ag distances of 3·72—3·93 Å and weak Ag–Br bonds of 2·68—2·96 Å in (**1**) and (**2**) *vs.* bonding Fe–Fe distances of 2·69—2·74 Å and normal Fe–S bonds of 2·20—2·30 Å in (**3**) and (**4**)] which are attributable to electronic effects, the most important similarity between the two systems is the trend of changes in average interatomic distances: M . . . M, X . . . X, M–X increases by 0·105, 0·052, 0·058 Å and 0·045, 0·128, 0·085 Å whereas the M–Y bond length decreases by 0·070 and 0·049 Å for the silver [(**1**) → (**2**)] and the iron [(**3**) → (**4**)] systems, respectively, in going from a dimer to a tetramer. Taking into consideration the change of formal oxidation state of 0·5 in going from the iron dimer [Fe(+3)] to the tetramer [Fe(+2·5)] but zero for the corresponding silver complexes, it is intriguing that the two trends are analogous. We believe that the small molecular parameter variations observed in going from the dimers to the corresponding tetramers are of no electronic consequence and, more importantly, that the oxidation states of the iron atoms in (**3**) and (**4**) are probably very similar.

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