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Sequential Growth of Heteropolymetallic ($Pt_2 \rightarrow AgPt_2 \rightarrow Ag_2Pt_2 \rightarrow Ag_2Pt_4$) Sulfide Aggregates. Structure of the Intermediate $Ag_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2$ with a Flat $\{Pt_2S_2\}$ Core and Two AgCl Molecular Pendants

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Introduction

The value of $Pt_2(PPh_3)_4(\mu\text{-}S)_2$ (**1**)[1] as a precursor to homo-,[2] hetero-,[3] and intermetallic[4] sulfide aggregates is exemplified by its ability to capture virtually all metal atoms in all common geometries. Such versatility, which is unmatched by other documented metalloligands,[5] is attributed to the high nucleophilicity and adjustable orientations of the sulfur lone pairs. Our recent studies[6] suggested that the lone pair directionality is a function of the dihedral angle of the $\{Pt_2S_2\}$ core. Among all the crystallographically established aggregates, this core is usually butterfly-shaped with the metals at the wing tips, S⋯S along the hinge, and the hinge angle range 123−139°.[2−4,7,8] Such butterfly configuration permits the lone pairs to point inward and therefore supports **1** as a chelating ligand. While this is commonly found, there are two notable exceptions, $[Au_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2]$ (**2**)[3d] and $[Ag_2\{Pt_2(PPh_3)_4(\mu\text{-}S)_2\}_2]^{2+}$ (**3**).[3b] Complex **3** is the only species whereby **1** is in a close-bridging mode in order to support an unusual Ag^I-Ag^I bond. Complex **2** contains a curiously flat $\{Pt_2S_2\}$ core; the significance of this structural anomaly was not realized until recently, when a large number of aggregates were crystallographically characterized and invariably all the $\{Pt_2S_2\}$ cores showed a butterfly structure.[2−4,7,8] Our objective therefore is to determine whether such a flat structure can be sustained when AuCl is replaced by its congeneric AgCl and whether the resultant complex is synthetically and/or structurally related to **3**. Accordingly, we wish to establish whether such folding of the butterfly is a necessary precondition to the switch of coordination mode from open- to close-bridging and whether these stereogeometrical changes could provide a platform for aggregate growth to occur. Our long-term target is to build supramolecular heterometallic structures from the existing metal aggregates. It is therefore pertinent to understand the structures and bonding of these aggregates and establish a growth mechanism.

Result and Discussion

Complex **1** reacts readily with equimolar $Ag(NO_3)(PPh_3)$ to give $[AgPt_2(PPh_3)_5(\mu_3\text{-}S)_2]NO_3$ (**4a**). The ionic nitrate group is verified by a strong IR band at 1384 cm^{-1} whereas molar conductivity measurements in MeOH show a 1:1 electrolyte. The Pt- and Ag-coordinated phosphines are identified from their $^{31}P\{^1H\}$ NMR resonances at a ∼4:1 intensity ratio with characteristic ^{195}Pt and $^{107}Ag/^{109}Ag$ couplings, respectively. Metathesis of **4a** with NH_4PF_6 gives $[AgPt_2(PPh_3)_5(\mu_3\text{-}S)_2]PF_6$ (**4b**). Mixing of $AgCl(PPh_3)$ with **1** in 2:1 molar ratio gives $Ag_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2$ (**5**), whose $^{31}P\{^1H\}$ NMR spectrum shows that there is no phosphine on the Ag(I) center and that all Pt-bound phosphines are equivalent. When equimolar amounts of $AgCl(PPh_3)$ and **1** are mixed, $[AgPt_2(PPh_3)_5(\mu_3\text{-}S)_2]Cl$, **4c**, and **5** are isolated. Complex **4c** is an intermediate in this reaction, and it converts to **5** in the presence of an equimolar amount of $AgCl(PPh_3)$. Complex **5** can also be prepared directly from **1** and AgCl in a heterogeneous reaction. Interestingly, an equimolar mixture of **5** and **1** readily gives $[Ag_2\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2\}_2]Cl_2$ (**3a**). This is effectively a ligand replacement reaction of chloride by the thio centers in **1**. There is no evidence for a metal migratory reaction such as the formation of $AgPt_2Cl(PPh_3)_4(\mu_3\text{-}S)$ (**6**) from **5**, but complex **6** can be prepared from **4c** via the ligand substitution of PPh_3 by Cl with stirring and heating. Complex **3a** metathesizes easily with NH_4PF_6 to give $[Ag_2\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2\}_2][PF_6]_2$ (**3b**). Similar hexametallic complexes of $[Ag_2\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2\}_2]X_2$ [X = NO_3^- (**3c**); BF_4^- (**3d**)][3b] have been prepared from the addition reactions of AgX with **1**. Complex **3a** reverts to **5** in the presence of excess $AgCl(PPh_3)$. These reactions show the strong affinity of Ag(I) for the thio ligands in **1**. The relationship of these reactions is summarized in Scheme 1.

Complex **4** represents a sulfide-bicapped triangular $AgPt_2$ aggregate whose Cu analogue, *viz.* $[CuPt_2(PPh_3)_5(\mu_3\text{-}S)_2]PF_6$,[3g] has been crystallographically characterized recently. Complex **3**, which was among the earliest aggregates reported, shows a hexametallic $\{Ag_2Pt_4\}$ structure with a strong Ag−Ag bond sandwiched by two $\{Pt_2S_2\}$ butterflies.[3b] It cannot be obtained from **4** through phosphine dissociation and dimerization but instead from a one-pot assembly of $[2Pt_2 + 2Ag^+]$ (*i.e.*, **1** + Ag^+) or an aggregate expansion reaction of $[Ag_2Pt_2 + Pt_2]$ (*i.e.*, **5** + **1**). A single-crystal X-ray diffraction analysis of **5** shows an intriguing planar $\{Pt_2S_2\}$ ring with two AgCl "molecular pendants" protruding out vertically from the sulfur sites at opposite directions. [Pt(1)−S(1)−Ag(1) = 82.5(1) and Pt(1a)−S(1)−Ag(1) = 80.0(1)°] (Figure 1) The *anti* arrangement of these two AgCl tails forbids any Ag−Ag interaction, which is in striking contrast to the Ag−Ag bond found in the T-shaped d^{10}-Ag(I) in **3**. Another notable difference is that the flat Pt planes in **5** hinge considerably in **3** (average $\theta = 138.6°$).[8] This "wing flapping" offers **1** an extra motional freedom which helps

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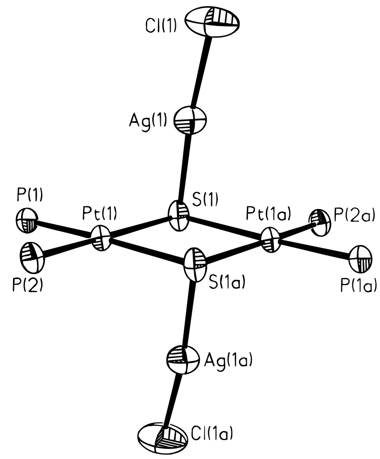
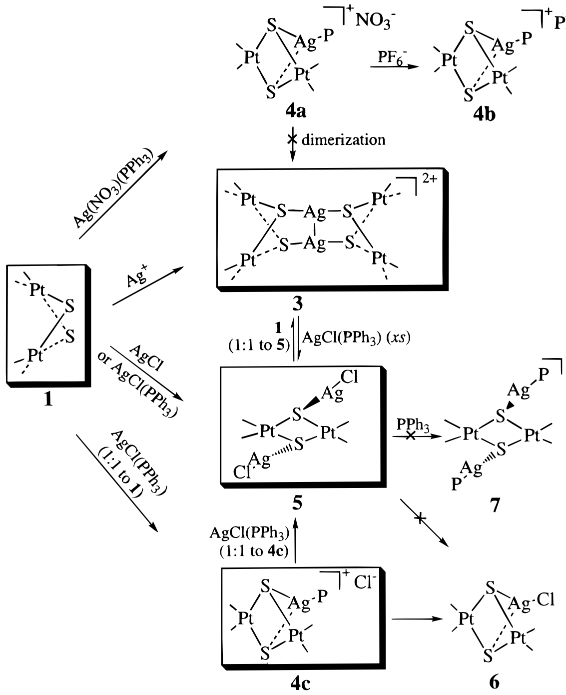


Figure 1. ORTEP plot of the molecular structure of $[Ag_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2]\cdot 2CHCl_3$ (**5**) with 50% probability thermal ellipsoids (phenyl rings and solvate removed for clarity).

Scheme 1. Heterometalation of $Pt_2(PPh_3)_4(\mu\text{-}S)_2$ (**1**) with Ag(I) Complexes Showing a Sequential Growth of the Boxed Structures (P = PPh_3)



to support a range of M−M distances. Conversion of **5** to **3** is therefore facile as it requires only chloride dissociation and closing up of the butterfly wings. Effectively, **1** changes from a chelating mode to an open-bridging and then a close-bridging mode in a sequential conversion from **4c** to **3** via **5**.

The short Ag···Pt separations in **5** [average 3.095(2) Å] are nonbonding although they are comparable with some longer Ag−Pt bonds found in the literature [*e.g.*, 2.772(3) and 3.063(3) Å in $(NBu_4)_2[Ag_2Pt_2(C_6F_5)_4Cl_4]$[9]]. Fenske−Hall molecular orbital calculations[10] on **5** did not reveal any orbital interactions.[11] The proximity of the heterometals is facilitated by the capping sulfides. Complex **5** shows no tendency to revert to **1** through fragmentation of AgCl. It is notable that, in the formation of **5** from **1** and excess $AgCl(PPh_3)$, phosphine preferentially departs and **5** is the thermodynamic sink. The covalence of the Ag−Cl bond in **5** is reflected in the strong bond [2.334(5) Å] and the fact that **5** shows little tendency to give **4** through phosphine substitution. There is also no evidence for the conversion of **5** to $[Ag_2Pt_2(PPh_3)_6(\mu_3\text{-}S)_2]Cl_2$ (**7**).

The $\{Pt_2S_2\}$ butterfly must fold in **4** because the heterometal is attached to both sulfur atoms.[6] The reason for this moiety being hinged in **3** but flat in **5** is less clear. It is established,[6] however, that when the $\{Pt_2S_2\}$ is hinged, the Pt coordination spheres and substituent−sulfur bonds are directly coupled; such coupling is absent when the core is flat since the M−S bonds are virtually perpendicular to the $\{Pt_2S_2\}$ core, as in **5**.

We think that, since the metalloligand initially donates electron density in order for the substituents to be attached to sulfur, the impetus for coupling in the presence of electron-donating groups would be to recoup some of the lost electron density. In support of our argument, we have performed Fenske−Hall[10] calculations on $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SCH_3)]^+$, which is hinged. The calculated Mulliken charges on the methyl carbon are −0.202 in the natural geometry and −0.246 when flat. In the case of **3**, although the Ag−Ag bond is electron withdrawing, the calculations indicate that the Ag atoms actually absorb more electron density when the $\{Pt_2S_2\}$ cores are flat: in the crystal structure (with phenyl rings replaced by H) the average Mulliken charge for Ag is +0.249, whereas for flat cores the value is +0.214. This suggests that coupling through folding allows the two $\{Pt_2S_2\}$ moieties to absorb some electron density from the Ag−Ag bond, which in turn is promoted by the electron-donating properties of the metalloligands themselves.

If the above hypothesis is correct, it is then not surprising that the core in **5** is flat, in view of the electron-withdrawing nature of the AgCl moiety. Of course, in the case of **3**, one must also not discount steric factors arising from the phenyl rings of the phosphine ligands, as well as the need for the S lone pairs to be tilted slightly inward for the Ag−Ag bond to form. (The inward tilt of Ag−S bond is too small to justify the relatively large amount of folding.)

Another point of interest is the *trans* binding of the AgCl fragments in **5**, rather than *cis* with an Ag−Ag bond and a folded $\{Pt_2S_2\}$ core, as in **3**. If the Ag−Ag bond is present, since Cl is more electron withdrawing, less electron density would reside in the bond, which becomes weaker as a consequence. Moreover, if, as suggested above, coupling is not favored by electron-withdrawing groups such as AgCl, there would be no impetus for folding of $\{Pt_2S_2\}$ simply for the formation of the relatively weak Ag−Ag bond, particularly in the face of electrostatic repulsion between the chloride ions. Note that, in **3**, the sulfur atoms are held in place by coordination to Pt and in any case, are less negatively charged.

Experimental Section

All reactions were performed in a nitrogen atmosphere. Elemental analyses were carried out in the Microanalytical Laboratory in our department. $^{31}P\{^1H\}$ NMR spectra were run on a Bruker ACF 300 spectrometer at 298 K with H_3PO_4 as external reference. IR spectra were taken in a KBr disk on a Perkin-Elmer 1600 FT-IR spectrophotometer. Solution conductivity was measured by using a STEM conductivity 1000 meter.

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Table 1. Crystallographic Data for $[Ag_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2]\cdot 2CHCl_3$ (**5**)

empirical formula	$C_{74}H_{62}Ag_2Cl_8P_4Pt_2S_2$
f_w	2028.8
space group	$P2_1/n$ (No. 14)
a	14.900(7) Å
b	14.148(6) Å
c	18.178(8) Å
β	100.51(4)°
V	3768(2) Å^3
Z	2
T	293 K
λ	0.71073 Å
D_{calcd}	1.788 g cm^{-3}
μ	4.679 mm^{-1}
no. of obsd rfclns	5205 [$F > 3\sigma(F)$]
R^a	0.056
$R_w{}^b$	0.095

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 × 10^3) of Selected Atoms for $[Ag_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2]\cdot 2CHCl_3$ (**5**)

atom	x	y	z	$U_{eq}{}^a$
Pt(1)	4151(1)	9910(1)	574(1)	22(1)
Ag(1)	6249(1)	9575(1)	1089(1)	48(1)
P(1)	3792(2)	10869(2)	1487(2)	26(1)
S(1)	5410(2)	10870(2)	459(2)	30(1)
P(2)	3083(2)	8745(2)	580(2)	29(1)
Cl(1)	7081(4)	8244(4)	1567(3)	88(2)

[a] Equivalent isotropic U_{eq} defined as one-third of trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Ag_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2]\cdot 2CHCl_3$ (**5**)[a]

Pt(1)−S(1)	2.356(3)	Pt(1)−S(1a)	2.370(4)
Ag(1)−S(1)	2.389(3)	Ag(1)−Cl(1)	2.333(6)
Pt(1)−P(1)	2.282(3)	Pt(1)−P(2)	2.293(3)
Pt(1)···Ag(1)	3.130(2)	Pt(1)···Ag(1a)	3.060(2)
Pt(1)···Pt(1a)	3.569(2)		
Pt(1)−S(1)−Pt(1a)	98.1(1)	Pt(1)−S(1)−Ag(1)	82.5(1)
Pt(1a)−S(1)−Ag(1)	80.0(1)	S(1)−Pt(1)−S(1a)	81.9(1)
S(1)−Pt(1)−P(1)	91.0(1)	S(1)−Pt(1)−P(2)	168.4(1)
S(1a)−Pt(1)−P(1)	171.2(1)	S(1a)−Pt(1)−P(2)	87.8(1)
P(1)−Pt(1)−P(2)	9.7(1)	S(1)−Ag(1)−Cl(1)	173.4(2)

[a] Symmetry operators: $1 - x$, $2 - y$, $-z$.

Synthesis of $[AgPt_2(PPh_3)_5(\mu_3\text{-}S)_2]^+$ (4) from 1. A mixture of **1** (0.150 g, 0.1 mmol) and $Ag(NO_3)(PPh_3)$ (0.043 g, 0.1 mmol) was stirred in THF (15 mL) for a few minutes to give a clear orange solution. Stirring was continued for 30 min and the resultant mixture filtered and treated with hexane (50 mL) to precipitate $[AgPt_2(PPh_3)_5(\mu_3\text{-}S)_2]NO_3$ (**4a**; 0.143 g, 75%). IR (cm^{-1}): 1384 s ($NO_3{}^-$). Molar conductivity Λ_m (10^{-3} M, MeOH): 87 Ω^{-1} cm^2 mol^{-1}. $[AgPt_2(PPh_3)_5(\mu_3\text{-}S)_2]PF_6$ (**4b**) was prepared by adding NH_4PF_6 to a MeOH solution of **4a**. $C_{90}H_{75}AgF_6P_6Pt_2S_2$ Anal. calcd: C, 53.5; H, 3.7; P, 9.2; S, 3.2. Found: C, 53.6; H, 3.8; P, 8.9; S, 3.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_{Pt} 22.3 [t, 4P, P−Pt, ^1J(P−Pt) = 2963 Hz, ^3J(P−Pt) = 24 Hz], δ_{Ag} = 12.6 [d, 1P, P−Ag, ^1J(P−^{107}Ag/^{109}Ag) = 577 Hz]. IR (cm^{-1}): 839 vs ($PF_6{}^-$).

Synthesis of $Ag_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2$ (5) from 1. To a suspension of **1** (0.15 g, 0.1 mmol) in THF (20 mL) was added with stirring $AgCl(PPh_3)$ (0.081 g, 0.2 mmol). After the suspension changed completely from orange to yellow, the suspended solid was isolated by filtration and purified by recrystallization from CH_2Cl_2/hexane to yield $Ag_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2$ (**5**) (0.099 g, 62%). It is insoluble in THF and MeOH but soluble in CH_2Cl_2 and $CHCl_3$. Single crystals of **5**·$2CHCl_3$ were obtained by slow evaporation of a solution of **5** in $CH_2Cl_2/CHCl_3$ (1:1). $C_{74}H_{62}Ag_2Cl_8P_4Pt_2S_2$ Anal. Calcd: C, 43.8; H, 3.1; Cl, 14.0; P, 6.1; S, 3.2. Found: C, 43.6; H, 3.0; Cl, 14.8; P, 6.5; S, 2.9. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.6 [t, ^1J(P−Pt) = 2883 Hz, ^3J(P−Pt) = 32 Hz].

The reaction was repeated using **1** (0.15 g, 0.1 mmol) and $AgCl(PPh_3)$ (0.040 g, 0.1 mmol). This resulted in a yellow suspension from which $[AgPt_2(PPh_3)_5(\mu_3\text{-}S)_2]Cl$ (**4c**; 0.087 g, 46%) and **5** (0.040 g, 21%) could be isolated from the mother liquor and residue, respectively.

Addition of $AgCl(PPh_3)$ (0.020 g, 0.05 mmol) to a solution of **4c** (0.096 g, 0.05 mmol) in THF (10 mL) with stirring gave arise to a yellow precipitate of **5** (0.041 g, 35%).

Complex **5** could be similarly obtained by stirring **1** (0.15 g, 0.1 mmol) with AgCl (0.028 g, 0.2 mmol) in THF (20 mL) (yield: 0.134 g, 75%).

Synthesis of $[Ag_2\{Pt_2(PPh_3)_4(\mu\text{-}S)_2\}_2]^{2+}$ (3) from 5 and 1. A suspension of **5** (0.095 g, 0.05 mmol) and **1** (0.075 g, 0.05 mmol) in THF (50 mL) was stirred for 2 h to give a clear orange solution from which yellow solid of $[Ag_2\{Pt_2(PPh_3)_4(\mu\text{-}S)_2\}_2]Cl_2$ (**3a**) could be isolated (0.068 g, 40%); Λ_m (10^{-3} M, MeOH) 158 Ω^{-1} cm^2 mol^{-1}. It was treated with NH_4PF_6 in MeOH to yield a yellowish green solid of $[Ag_2\{Pt_2(PPh_3)_4(\mu\text{-}S)_2\}_2](PF_6)_2$ (**3b**). Evaporation of a solution of **3b** in CH_2Cl_2/MeOH yielded crystals of $[Ag_2\{Pt_2(PPh_3)_4(\mu\text{-}S)_2\}_2](PF_6)_2$. Anal. Calcd: C, 49.2; H, 3.5; P, 8.8; S, 3.6. Found: C, 48.5; H, 4.0; P, 8.2; S, 3.4. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 20.0 [t, ^1J(P−Pt) = 2924 Hz].

Crystal Structure Determination. A suitable single crystal of **5** with dimensions of 0.26 × 0.33 × 0.45 mm was chosen for X-ray diffraction analysis. Data collection was carried out at 293 K with Mo Kα radiation (λ = 0.710 73 Å) on a Siemens R3m/V diffractometer equipped with a graphite monochromator and $\omega - 2\theta$ scan mode. A summary of the data collection and structure refinement parameters is given in Table 1. The data were corrected for Lorentz and polarization effects; semiempirical absorption correction was also applied. The structure was solved by direct methods and difference Fourier maps. Full-matrix least-squares refinement was carried out with anisotropic temperature factor for all non-hydrogen atoms. Phenyl rings were fixed, and hydrogen atoms were place on calculated positions (C−H 0.96 Å) and assigned isotropic thermal parameters riding on their parent atoms. Initial calculations were performed on a PC using SHELXTL PC software package; SHELXTL-93[12] was used for the final refinement.

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Supporting Information Available: Listing of detailed crystallographic data, refined atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, and least-squares plane (9 pages). Ordering information is given on any current masthead page.

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