

## First Examples of Au<sup>I</sup>-X-Ag<sup>I</sup> Halonium Cations (X = Cl and Br)

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Received March 9, 2003; E-mail: chmyiphk@nus.edu.sg

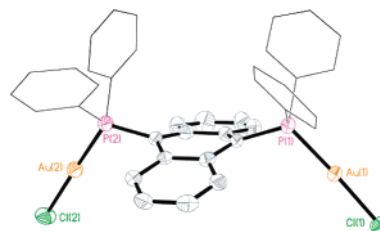
Silver(I) ion has strong affinity for soft halides (X' = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>). This property has long been harnessed to remove the poor leaving halide ligand from a metal complex [M - X']<sup>n+</sup> (eq 1, Y = anion).<sup>1</sup>



The stability and spontaneous precipitation of AgX' from the solution drive the equilibrium toward the complex [M]<sup>(n+1)+</sup>Y<sup>-</sup> which would react readily with an incoming ligand.<sup>1</sup> This simple synthetic strategy has been used to generate the (R<sub>3</sub>PAu)<sup>+</sup> ion from R<sub>3</sub>PAuCl (R = aryl or alkyl).<sup>2</sup> The ion, a powerful aurating agent, has been used extensively in synthesizing metal clusters, especially polygold(I) complexes.<sup>3</sup> An example related to the present study is the formation of the novel [digold(I)]halonium cations [(R<sub>3</sub>PAu)<sub>2</sub>X']<sup>Y</sup> (Y = ClO<sub>4</sub><sup>-</sup>,<sup>4</sup> BF<sub>4</sub><sup>-</sup>,<sup>5a</sup> SbF<sub>6</sub><sup>-5b,c</sup>) from the coordination of (R<sub>3</sub>PAu)<sup>+</sup> to the halide in R<sub>3</sub>PAuX'. Interestingly, recent studies showed that when SbF<sub>6</sub><sup>-</sup> is the counterion, the halonium ion would dimerize into {(PPh<sub>3</sub>PAu)<sub>2</sub>X'}<sub>2</sub><sup>2+</sup> via aurophilic attractions.<sup>5b,c</sup> However, there are notable exceptions where silver halides are found incorporated into the final clusters, i.e., [(p-tol<sub>3</sub>P)<sub>12</sub>Au<sub>18</sub>Ag<sub>20</sub>Cl<sub>14</sub>],<sup>6a</sup> and interestingly, both AgCl and (PPh<sub>3</sub>-Au)<sup>+</sup> ions, produced from the reaction of AgNO<sub>3</sub> with PPh<sub>3</sub>AuCl, are assembled in the cluster [Pt<sub>3</sub>(μ<sub>3</sub>-S)(AuPPh<sub>3</sub>)(μ<sub>3</sub>-AgCl)(μ-PH<sub>2</sub>-PCH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>]<sup>+</sup>.<sup>6c</sup> Usón et al.<sup>7</sup> demonstrated that the reactions between organoplatinum halides and Ag<sup>I</sup> ion give rise to complexes which contain [Pt-X-Ag] linkage (X = Cl, Br). Remarkably, the structures of the complexes implicate the existence of Pt → Ag bonding. In this communication, we report a new reaction between Ag<sup>I</sup> and phosphinegold(I) halides: instead of precipitating AgX, the reactions of (μ-PANP)(AuX)<sub>2</sub> (PANP = 9,10-bis(diphenylphosphino)anthracene,<sup>8</sup> X = Cl and Br) with 1/2 mol equiv of AgSbF<sub>6</sub> were found to give rise to unprecedented Au<sup>I</sup>-X-Ag<sup>I</sup> halonium cations (Scheme 1).

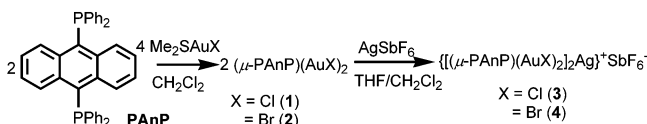
Reacting PANP with 2 mol equiv of Me<sub>2</sub>SAuX gives the binuclear complexes (μ-PANP)(AuX)<sub>2</sub> (X = Cl, **1**; = Br, **2**). The X-ray crystal structures of **1**·1/2Et<sub>2</sub>O (Figure 1) and **2**·Et<sub>2</sub>O (SI) show a PANP coordinating to two linear syn-oriented P-Au-X groups (av P-Au-Cl angle = 177.65(6)°, av P-Au-Br angle = 177.43(4)°). The Au-P and Au-X bond lengths of the compounds are typical for the phosphinegold(I) halides. The two Au atoms are widely separated by 9.154(2) Å (**1**) and 9.091(4) Å (**2**). To relieve the steric repulsion with the phenyl rings, the anthracenyl rings in **1** and **2** are slightly curved toward the Au-X units. The dihedral angles between the two lateral benzene rings are 23.0° and 24.2° for **1** and **2**, respectively.

While reacting **1** and **2** with 2 mol equiv of AgSbF<sub>6</sub> leads to spontaneous precipitation of AgX and formation of [(μ-PANP)-Au<sub>2</sub>]<sup>2+</sup> ion, slow diffusions between a CH<sub>2</sub>Cl<sub>2</sub> solution of (μ-PANP)(AuX)<sub>2</sub> and a THF solution of 1/2 mol equiv of AgSbF<sub>6</sub> give yellow crystals of {[(μ-PANP)(AuX)<sub>2</sub>]<sub>2</sub>Ag<sup>+</sup>SbF<sub>6</sub><sup>-</sup>·2CH<sub>2</sub>Cl<sub>2</sub>} (X = Cl, **3**·2CH<sub>2</sub>Cl<sub>2</sub>; X = Br, **4**·2CH<sub>2</sub>Cl<sub>2</sub>) as products. Both compounds



**Figure 1.** ORTEP plot of **1** in crystals of **1**·1/2Et<sub>2</sub>O (thermal ellipsoid = 50%). All the H atoms and Et<sub>2</sub>O are removed for clarity.

### Scheme 1



crystallize in the tetragonal space group *I4/m*. X-ray crystal analysis revealed that **3** (Figure 2) and **4** (SI) are isostructural, being composed of helical coordination polymers of (μ-PANP)(AuX)<sub>2</sub> and Ag<sup>I</sup> ions. The SbF<sub>6</sub><sup>-</sup> ions have no contact with the polymer chains. Notably, the (μ-PANP)(AuX)<sub>2</sub> molecules undergo pronounced conformational changes in forming compounds **3** and **4**: the anthracenyl rings are slightly curved away from the Au atoms, and the P-Au-X units are tilted toward one end of the anthracenyl ring (Figure 2b). The dihedral angles between the lateral benzene rings in **3** and **4** are 18.8° and 17.9°, respectively. Because of the distortion, the two P-Au-X units are drawn closer and the Au-Au distances are shortened to 7.737(2) and 7.768(1) Å in **3** and **4**, respectively. The large structural changes suggest that the anthracenyl backbone of the ligand is highly flexible. The conformational changes facilitates π-π interactions between two (μ-PANP)(AuX)<sub>2</sub> molecules whose anthracenyl rings overlap partially with separations typical for aromatic π-π stacking (3.627(2) Å (**3**) and 3.618(2) Å (**4**)).<sup>9</sup> Intriguingly, the Au and X atoms of four neighboring (μ-PANP)(AuX)<sub>2</sub> molecules constitute the vertices of a *distorted dodecahedron* (Figure 2c). Encapsulated at the center of the polyhedron is a silver(I) ion. Because of the different Au-X distances, the symmetry of the dodecahedron degenerates from the maximum *D<sub>2d</sub>* to *S<sub>4</sub>*. The Au<sub>4</sub>X<sub>4</sub> dodecahedron can be also called bisdiphenoids as it comprises two interpenetrating Au<sub>4</sub> and X<sub>4</sub> tetrahedra. The four halides coordinate weakly to the central Ag<sup>I</sup> ion, showing long Ag-X bond distances (Ag-Cl = 2.624(2) Å, Ag-Br = 2.7137(1) Å). The compounds feature the first examples of (Au<sup>I</sup>-X)<sub>4</sub>Ag<sup>I</sup> halonium ions which are nonclassical as the halides bear a fractional formal charge of +1/4. The AgX<sub>4</sub> tetrahedra are distorted with Cl-Ag-Cl angles of 115.00(5)° and 98.90(9)° and Br-Ag-Br angles of 114.18(3)° and 100.42(5)°. On the other hand, the distortion in the AgAu<sub>4</sub> tetrahedra is more severe: the Au-Ag-Au angles in **3** and **4** are 126.385(9)°, 79.2569(2)° and 127.168(1)°, 77.977(2)°, respectively. The shortest Au-Au distances in the dodecahedra, 4.105(2) Å (**3**) and 4.115(2) Å (**4**), are



**Figure 2.** (a) ORTEP plot of  $3 \cdot 2\text{CH}_2\text{Cl}_2$  (thermal ellipsoid = 50%). All H atoms, solvent and anions are not shown. (b) Compound **3** viewed along  $c$ -axis. All phenyl rings are not shown. (c) Diagram showing the  $\text{AgAu}_4\text{Cl}_4$  dodecahedron; the solid lines indicate bonding interactions and the broken lines show the faces of the dodecahedron.

too long for aurophilic interactions. The Au–X bonds ( $X = \text{Cl}$ , 2.313(2) Å;  $= \text{Br}$ , 2.4171(1) Å) are basically unaffected by the Ag–X coordination as they are only slightly longer than the corresponding ones in **1** (2.2975(2) Å) and **2** (2.3924(7) Å). As the coordinated halides are known as poor electron donors and  $\text{Ag}^{\text{I}}$  ion as a strong electron acceptor, the halonium ions can be regarded as strong Lewis acid and weak Lewis base adducts.<sup>10</sup> While the Au–P bonds of **3** and **4** (2.241(2) Å) have the same length, the Au–X and Ag–X bonds are elongated significantly as X is changed from Cl to Br (Au–Cl = 2.313(2) Å, Au–Br = 2.4171(1) Å, Ag–Cl = 2.624(2) Å, Ag–Br = 2.7137(1) Å). Surprisingly the Au–Ag distance does not show a proportional increase: the unusually acute Au–Cl–Ag angle of 81.08(7)° leads to the Au–Ag separation of 3.2180(4) Å in **3**, and further compressed Au–Br–Au of 79.04(4)° in **4** keeps a very similar Au–Ag of 3.2701(5) Å. Notably, exceedingly small Pt–X–Ag angles are observed in  $\{[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-Cl})_2\text{Ag}]_2\}^{2-}$  (65.9(2)°)<sup>7a</sup> and  $[(\text{L})\text{Pt}(\mu\text{-Br})\text{Ag}(\text{PPh}_3)]$  ( $\text{L} = (\text{Ph}_3\text{P})(\text{C}_6\text{C}_{15})\text{Br}$ ) (70.6(1)°)<sup>7b</sup> which are crucial in fostering Pt–Ag bonding. It is therefore believed that  $\text{Au}^{\text{I}}\text{-Ag}^{\text{I}}$  metallophilic interactions may play a role in stabilizing the halonium complexes. Closed-shell interactions are responsible for the assembling of heavy  $d^{10}$  metal complexes in solid state.<sup>11</sup> Although the Au–Ag distances in **3** and **4** are on the long end of the reported  $\text{Au}^{\text{I}}\text{-Ag}^{\text{I}}$  bond distance (2.8–3.3 Å),<sup>12</sup> they are shorter than the sum of the van der Waals radii of the metals (3.4 Å)<sup>13</sup> and lie within the range of Au–Ag bond distances proposed by theoretical calculations.<sup>12c</sup> Another structural feature lending support to the existence of Au–Ag interactions is the bending of the P–Au–X units toward the central  $\text{Ag}^{\text{I}}$  ion, illustrated by the fact that the P–Au–X angle in the halonium ions ( $X = \text{Cl}$ , 174.98(5)°;  $= \text{Br}$ , 173.60(9)°) are smaller than the corresponding ones in the **1** (177.65(6)°) and **2** (177.43(4)°).

On the basis of these structural features, the halonium cations are believed to be stabilized by the collective actions of Ag–X and Au–Ag and  $\pi$ – $\pi$  interactions. This could be the reason the formation of the halonium cations is favored over that of halide abstraction. The robustness of the polymers is suggested by the insolubility of **3** and **4** in most of the organic solvents except DMSO. The  $^31\text{P}\{^1\text{H}\}$  NMR spectra of **3** and **4** measured in DMSO- $d_6$ , which show a singlet at  $\delta$  26.85 and 28.82, respectively, are identical to those of **1** and **2**. In addition, the halide abstraction could be disfavored by the low Ag<sup>I</sup>/X ratio of 1/4 in the reactions as the Lewis acidity of  $\text{Ag}^{\text{I}}$  ion is expected to be attenuated by the coordination of four halide ions. Investigations of the effect of

phosphines and anions on the structures and stability of the halonium cations are now underway in our laboratory.

**Acknowledgment.** We thank the National University of Singapore for financial support.

**Supporting Information Available:** Experimental procedures and X-ray crystal structures of  $2 \cdot \text{Et}_2\text{O}$  and  $4 \cdot 2\text{CH}_2\text{Cl}_2$  (PDF). Crystal data and CIF files of  $1 \cdot 1/2\text{Et}_2\text{O}$ ,  $2 \cdot \text{Et}_2\text{O}$ ,  $3 \cdot 2\text{CH}_2\text{Cl}_2$ , and  $4 \cdot 2\text{CH}_2\text{Cl}_2$ . This material is available free of charge via the Internet at <http://pubs.acs.org>

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JA035064Z