

## Metallophilicity: The Dimerization of Bis[(triphenylphosphine)gold(I)]chloronium Cations

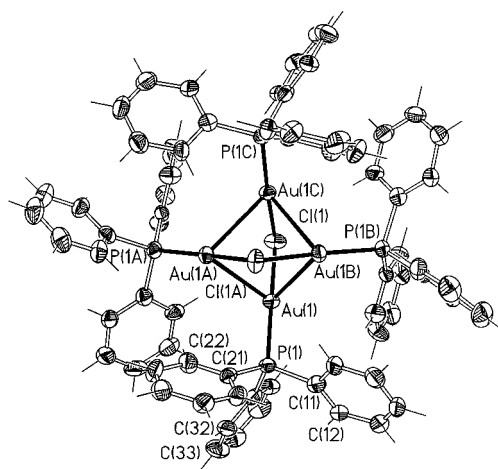
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The current literature reflects a rapidly growing interest in closed-shell interactions between the metal centers of complexes of the heavy late transition elements.<sup>1</sup> The effects of 5d<sup>10</sup>–5d<sup>10</sup> interactions on structure and bonding of such complexes are particularly obvious for coordination compounds of gold(I) (“aurophilicity”),<sup>2</sup> but similar phenomena have been reported for several of the neighboring elements of gold in the Periodic Table (“metallophilicity”).<sup>3</sup> It appears that weak attractive forces between metal atoms or cations with seemingly saturated electron configurations play an important role in determining the configuration, conformation, and oligomerization of complexes.<sup>4</sup>

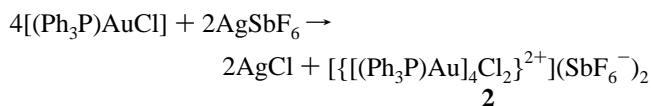
In this communication we report the unprecedented *dimerization* of the bis[(triphenylphosphine)gold(I)]chloronium cation in its hexafluoroantimonate(VI) salt. Salts with this chloronium cation  $[(\text{Ph}_3\text{P})\text{Au}_2\text{Cl}]^+\text{X}^-$  were first observed by Uson et al. in 1979.<sup>5</sup> The crystal structure of the perchlorate salt (**1**, containing 1 mol equiv of  $\text{CH}_2\text{Cl}_2$ ) was determined by Jones et al. in 1980, and the cation was shown to be *monomeric* and to have the expected angular structure<sup>6</sup> which is similar to that of the neutral, isoelectronic sulfide and selenide complexes  $[(\text{Ph}_3\text{P})\text{Au}_2\text{S/Se}]$ .<sup>7–9</sup> The angles Au–Cl–Au in **1** were found to be extremely small [80.7 and 82.7° for two independent cations in the unit cell] and to be associated with short aurophilic contacts of 3.035 and 3.085 Å, respectively.<sup>6</sup> The corresponding bromonium tetrafluoroborate



**Figure 1.** Molecular structure of a dication in  $[\{[(\text{Ph}_3\text{P})\text{Au}_4\text{Cl}_2]^{2+}\}(\text{SbF}_6^-)_2]$ , **2**, with atomic numbering (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). The asymmetric unit contains two independent dications of  $S_4$  symmetry with very similar dimensions, of which only one is shown. Selected bond lengths [Å] and angles [deg] (with the second decation in brackets): Au1–Au1A 3.0734(4) [3.0788(4)], Au1–P1 2.250(2) [2.252(2)], Au1–Cl1 2.355(2) [2.366(2)], P1–Au1–Cl1 170.99(8) [171.12(7)], Au1–Cl1–Au1C 101.4(1) [102.0(1)], Au1A–Au1–Au1B 72.73(1) [73.38(1)].

salt was recently reported from this laboratory<sup>10</sup> and showed an analogous structure, but with an Au–Br–Au angle of 96.83(3)° and a correspondingly longer Au–Au contact of 3.6477(1) Å. This work also included chloronium salts with phosphines other than  $\text{Ph}_3\text{P}$ .<sup>9,10</sup> The present work is also important, because it describes some of the most stable halonium ions reported so far.<sup>11</sup>

Treatment of  $(\text{Ph}_3\text{P})\text{AuCl}$  with only *half* a mole equivalent of  $\text{AgSbF}_6$  in tetrahydrofuran/dichloromethane at  $-78^\circ\text{C}$  under protection against incandescent light leads to the precipitate of  $\text{AgCl}$  and a clear colorless solution. Filtration and partial evaporation of the solvents from the filtrate under vacuum give colorless crystals in 84% yield, which were identified as  $[\{[(\text{Ph}_3\text{P})\text{Au}_4\text{Cl}_2]^{2+}\}(\text{SbF}_6^-)_2]$  (**2**):



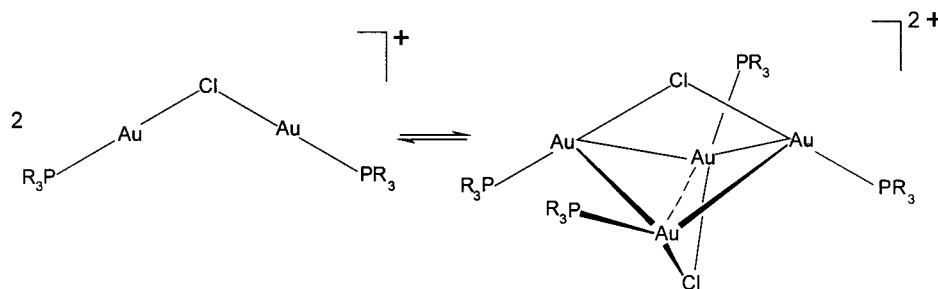
Solutions of compound **2** in trichloromethane-*d* show only one <sup>31</sup>P resonance in the NMR spectrum with a chemical shift (31.62 ppm) similar to that of **1** (31.50 ppm).<sup>10</sup> In the <sup>1</sup>H and <sup>13</sup>C NMR spectra there is only one set of phenyl resonances indicating equivalent phenyl groups in solution. In the mass spectrum of the compound (FD) the cation  $[(\text{Ph}_3\text{P})\text{Au}_2\text{Cl}]^+$  is the parent peak at  $m/z$  955 (<sup>37</sup>Cl).<sup>12</sup>

Crystals of **2** (from dichloromethane/pentane)<sup>13</sup> are tetragonal, space group  $I\bar{4}$ . Surprisingly, the lattice is composed of *tetra-nuclear dications* (Figure 1) and hexafluoroantimonate anions. There are two different dications each with crystallographically imposed  $S_4$  symmetry and with very similar geometrical details (caption to Figure 1). Two quarters taken from two different dications therefore represent the asymmetric unit of the crystal. The gold atoms are at the corners of a bisphenoid with contacts Au1–Au1\* 3.0734(4) and Au2–Au2\* 3.0788(4) Å in the two

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**Scheme 1.** Dimerization of Two Digoldchloronium Cations  $\{[(R_3P)Au]_2Cl\}^+$ 

independent dications. The arrangement of the four gold atoms may also be described as two edge-sharing triangles with an angle between two planes of  $94.8^\circ$  and  $96.3^\circ$ , respectively (dashed line in Scheme 1). Each of the chlorine atoms is spanning two opposite gold atoms with angles  $Au1-Cl1-Au1^*$   $101.4(1)^\circ$  and  $Au2-Cl2-Au2^*$   $102.0(1)^\circ$  and transannular metal-metal distances of  $Au1-Au1^{**}$   $3.645 \text{ \AA}$  and  $Au2-Au2^{**}$   $3.679 \text{ \AA}$ .

An inspection of the structure shows that two dinuclear chloronium cations (as found in **1**)<sup>6</sup> have undergone an intimate aggregation (Scheme 1). This association is drastically affecting the structure of the monomeric units as shown most clearly by a widening of the  $Au-Cl-Au$  angle by no less than  $20^\circ$ , from  $81.7^\circ$  in **1** to  $101.7^\circ$  in **2** (average). The newly formed inter-cationic  $Au-Au$  contacts in the dimer ( $3.075 \text{ \AA}$ , average) are virtually the same, however, as the intramolecular contacts in the monomer (**1**:  $3.065 \text{ \AA}$ ). It should be noted that the dimerization occurs against electrostatic repulsion, which appears to be offset by the gain in the number of aurophilic interactions (2 vs 4).

There are no conspicuous contacts between dications and anions in the lattices of compounds **1** and **2**. The different degree of

oligomerization in the two compounds may therefore be ascribed to differences in the general (nondirectional) lattice energy. Recent quantum-chemical calculations (relativistic DFT)<sup>14</sup> on the dimerization of the related oxonium cations of the type  $\{[(R_3P)Au]_2O\}^+$  have shown that the distribution of charge in the lattice has a great influence on the mode of association and the stability of the resulting polynuclear units. With small monoanions [ $ClO_4^-$  in **1**], ionic lattices with an equal number of *monocations* are preferred over the combination with only half the number of *dications*, while for larger anions [ $SbF_6^-$  in **2**] the dimerization of the anions is supported by the lattice.

The spectroscopic data of the solutions of **2** indicate that the tetranuclear dications are dissociated into the conventional dinuclear monocations by solvation in dichloromethane, which again confirms the importance of the lattice electrostatics for the aggregation of the components. As a more general conclusion our results show that the unexpected absence of metallophilic interactions in an ionic solid<sup>6</sup> (as in **1**) or in solution may only be a consequence of the relative lattice energies (solvation energies). A change of counterion (solvent) may be sufficient to induce fundamental changes.

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**Supporting Information Available:** Displacement ellipsoid plot, tables of crystal data, structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic parameters for **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) Preparation: A solution of  $(Ph_3P)AuCl$  (240 mg, 0.485 mmol) in dichloromethane (20 mL) is slowly added under stirring at  $-78^\circ C$  and protection against incandescent light to a slurry of  $AgSbF_6$  (83.3 mg, 0.243 mmol) in tetrahydrofuran (20 mL). A precipitate of  $AgCl$  is formed, which, after having been stirred for another 2 h and warmed up to ambient temperature, is removed by filtration. The volume of the filtrate is reduced to 3 mL under vacuum and pentane is added to precipitate the product (242 mg, 84% yield, after drying in a vacuum, mp  $142^\circ C$  dec). Elemental analysis: found C 36.36, H 2.54; calcd. for  $C_{36}H_{30}Au_2ClF_6P_2Sb$  (1189.84) C 36.80, H 2.58.

(13) Crystallographic data for **2**:  $C_{36}H_{30}Au_2ClF_6P_2Sb$  crystal system tetragonal, space group  $I4$ ,  $a = 25.7515(2) \text{ \AA}$ ,  $c = 13.9439(2) \text{ \AA}$ ,  $T = 163(2) \text{ K}$ ,  $Z = 8$ ,  $R_1 = 0.0384$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.0934$  (all data),  $GoF = 1.033$ . The crystal was an inversion twin with a contribution of the minor component at 0.232(6). The twinning was modeled by the respective routines in the SHELX97 program.<sup>15</sup> The scattering contributions of a highly disordered dichloromethane molecule in **2** were taken into account by using the SQUEEZE method followed by an absorption correction with DELABS. Both procedures are part of the PLATON suite of programs.<sup>16</sup>

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