Preparation and Structure of Poly(gold)telluronium Salts

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Telluronium Complexes, Gold(I) Complexes, Tri- and Tetra(gold)telluronium Salts, Auriophilicity, Crystal Structure

Tris[(triphenylphosphine)gold(I)]telluronium tetrafluoroborate (1) was prepared from the corresponding oxonium salt and bis(β-butyldimethylsilyl)tellurium in dichloromethane at −78 °C. The product forms yellow crystals, thermally stable to 125 °C. It was identified by standard analytical and spectroscopic techniques, including a single crystal X-ray diffraction study. In the crystal lattice, the cations form tellurium-capped triangles of gold, which are associated into dimers through short intermolecular Au–Au contacts, resembling those in the corresponding sulfur and selenium compounds. – The reaction of (β-BuMe₂Si)₂Te with four equivalents of [(Ph₃P)Au]BF₄ in tetrahydrofuran at −78 °C gives a tetranuclear compound, [((Ph₃P)Au)₄Te]⁺ 2 BF₄⁻ (2) which differs from 1 in its analytical and spectroscopic data. Its structure could not be determined, but it is assumed that the dications have a square pyramidal geometry.

Introduction

Gold has a very special affinity to tellurium. In the world of minerals, tellurium is the only metalloid to form binary compounds with gold [1]. Binary anionic species have recently been prepared in a variety of stoichiometries and structures, which show a unique relationship of the two elements [2–7]. Gold organotellurides (R₆TeAu)ₙ and their complexes were prepared only recently and our knowledge is limited to compounds with very bulky substituents [8,9].

The current interest in the gold/tellurium system arises from a relevance of pertinent research for semiconductor technology, material science, and pharmacology. This resembles the situation with the analogous selenium- and sulfur/gold systems, for which extensive investigations were initiated at a much earlier stage.

Complex units LₐAu⁺ (with L a standard electron donor ligand) are known to aggregate at sulfide or selenide centers (E₂⁻) to give mono-, di-, tri-, and finally tetranuclear coordination compounds of the type [(LAu)ₙE]^{[n–2]+} [10–12]. These units can be further aggregated into dimers or polymers through Au–Au contacts (auriophilicity [13]). For E = Te only very few examples of this series have been confirmed [8,9], and we have therefore become engaged in a study oriented towards the synthesis of the species with n = 3, 4 which are most prominent for E = S, Se [10–12].

Results

The preparative methods providing access to poly(gold)telluronium salts can be adopted from previous studies with the corresponding sulfonium and selenonium salts. The key reaction for the tri- and tetranuclear compound is the treatment of the oxonium salt with a disilyl chalcogenide (R₃Si)₂E in dichloromethane at −78 °C.

While the trimethylsilyl compounds proved most useful in the sulfur and selenium series, the more stable t-butyldimethylsilyl homologues offered distinct advantages in the tellurium case. For L = Ph₃P the isolated yield of product 1 was 33%. With L = Me₃P only decomposition products were obtained.

\[ [(\text{Ph₃P})\text{Au})₃\text{O}]^+ \text{BF}_4^- + (\text{β-BuMe₂Si})₂\text{Te} \rightarrow \]
\[ (\text{β-BuMe₂Si})₂\text{Te} + [(\text{Ph₃P})\text{Au})₄\text{Te}]^+ \text{BF}_4^- \]

(1)

Compound 1 forms yellow crystals, m.p. 125–127 °C with decomposition, soluble in chloroform and dichloromethane. In the Fast Atom Bombardment mass spectrum (nitrobenzyl alcohol matrix) the mass of the cation is observed as the parent

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Table II. Selected atomic distances [Å] and bond angles [°] in the structure of compound 1. (See Figures 1 and 2; standard deviations in parantheses).

-78 °C afforded a yellow crystalline product (2) in good yield (54%):

\[
4[(\text{Ph}_3\text{P})\text{Au}]\text{BF}_4 + (\text{t-BuMe}_2\text{Si})_2\text{Te} + 2\text{thf} \rightarrow 2\text{t-BuMe}_2\text{SiF} + 2(\text{thf})\text{BF}_3 + [(\text{Ph}_3\text{P})\text{Au}]_2\text{Te}^2^+ (\text{BF}_4^-)_2 (2)
\]

The compound decomposes at 103–104 °C and is soluble in di- and trichloromethane. The Field Desorption mass spectrum shows the cation with \( m/z = 1504 \) as the parent peak, which can be assigned to the trinuclear cation as a stable fragment. In the \( ^{31}\text{P}[^1\text{H}] \) NMR spectrum of CDC\(_1\) solutions only one sharp signal is observed, with a chemical shift \( \delta = 39.2 \text{ ppm} \), distinctly different from that of compound 1 (\( \delta = 37.9 \text{ ppm} \)). The \(^1\text{H} \) NMR spectrum has a phenyl multiplet with a specific fine structure not identical with that of 1. The elemental analysis data are in good agreement with the values calculated for the proposed formula (2), and therefore there is good reason to assume that the product of reaction (2) is the tetrafluoroborate salt of the tetranuclear telluronium dication (2).

The analogous oxygen [14] and sulfur compounds [15,16] have recently been prepared. The former has a standard tetrahedral structure, but the latter was found to have the dications in a non-classical square pyramidal configuration.

There is an analogy for this non-conformal behaviour in the pnictogen series, where the tetra(gold)ammonium cations are tetrahedral, while tetra(gold)phosphonium and -arsenium cations are square pyramidal [16,17].

To a solution of the oxonium salt (0.25 g, 0.17 mmol) in dichloromethane (20 mL) was added a solution of (t-BuMe\(_2\)Si)\(_2\)Te (0.12 g, 0.33 mmol) in tetrahydrofuran (10 mL) at −78 °C. After stirring for 60 min, the product was precipitated by careful addition of pentane (15 mL). The precipitate was recrystallized from dichloromethane/diethyl ether, yield 0.09 g (33%), yellow crystals, dec. temp. 125–127 °C. \(^1\text{H} \) NMR (CDC\(_3\), −60 °C): \( \delta = 7.2–7.5 \text{ ppm} \), m. Ph. \( ^{13}\text{C}[^1\text{H}] \) NMR (CDC\(_3\), −60 °C): \( \delta = 128.7 \text{ ppm [d, } J(\text{PC}) = 45.1 \text{ Hz, C1}], 129.4 \text{ [d, } J(\text{PC}) = 10.1, \text{ C3/5}], 131.9 \text{ (s, C4), 133.3 [d, } J(\text{PC}) = 15.2, \text{ C2/6)].} ^{31}\text{P}[^1\text{H}] \) NMR (CDC\(_3\), −60 °C): \( \delta = \)}
37.9 (s). MS (FAB, nitrobenzyl alcohol): m/z = 1505 (M⁺, 17%).

C₅₄H₄₉Au₂BF₄P₂Te (1592.18)
  Calcd C 40.73 H 2.85 Te 8.01%,
  Found C 38.83 H 2.66 Te 8.52%.

Crystal structure determination: Details of the structural work are summarized in Table I. Supplementary material has been deposited at Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (CSD 59235).

Tetrakis[(triphenylphosphine)gold(I)]-telluronium (2⁺) bis[tetrafluoroborate (-1)] (2)

To a solution of [(Ph₃P)Au]BF₄ (1.08 g, 2.34 mmol) in tetrahydrofuran (80 mL) was added a solution of (t-BuMe₂Si)₂Te (0.21 g, 0.59 mL) in tetrahydrofuran (10 mL) at -78 °C. After stirring for 30 min the solution was allowed to warm to ambient temperature. A part of the solvent was removed in a vacuum (ca. 50 mL) and the product precipitated from the remaining solution by carefully adding pentane (ca. 10 mL), yield 0.68 g (54%), colourless crystals, dec. temp. 103-104 °C.

'H NMR (CDCl₃, -60°C): δ = 7.0-7.5 ppm (m, Ph).

3¹P{'H} NMR (CDCl₃, -60°C): δ = 39.2 (s).

MS (FD, CFLC₁₂): m/z = 1505 (M⁺-AuPPh₃, 14%).

C₇₃H₆₀Au₄B₁₂F₆P₄Te (2138.26)
  Calcd C 40.44 H 2.83 Te 5.97%,
  Found C 41.58 H 3.12 Te 5.70%.

References:
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[19] From equimolar quantities of Ph₃PdCl and AgBF₄ in tetrahydrofuran at -78 °C. After 2 h of stirring, the precipitate is allowed to settle, and the solution is decanted.