Bridging of Trigoldsulfonium Clusters by a Silver(I) Ion

Alexander Sladek, Hubert Schmidbaur
Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany
Z. Naturforsch. 52b, 301–303 (1997); received January 3, 1997
Gold Clusters, Silver Bridging, Sulfonium Cations, Mixed Gold/Silver Cluster

Treatment of tris[(triphenylophosphine)gold(I)]-sulfonium tetrafluoroborate with AgBF₄ (molar ratio 2:1) in tetrahydrofuran affords a heptanuclear mixed-metal cluster trication [{[(Ph₃P)₆Au₆AgS₂](thf)}⁺⁺⁺ as the tetrafluoroborate salt. The crystal structure of the compound has been determined by X-ray diffraction. The silver atom is found in a bridging position between the two Au₃S units with short contacts to both sulfur atoms and to three out of six gold atoms. The coordination sphere of the silver atom is complemented by a tetrahydrofuran molecule. In di(tri)chloromethane solutions there is rapid site exchange of the silver coordination as shown by virtual equivalence of the phosphine ligands on the NMR time scale at ambient temperature.

Introduction

Sulfide anions S²⁻ are efficient clustering centers for gold(I) cations. Depending on the stoichiometry of the reactions stable products with various S/Au ratios have been found, including monosulfur species of the type [S(AuL)₂], [S(AuL)₃]⁺ and [S(AuL)₄]²⁻ where the gold atoms carry stabilizing metal-metal bonding for these moieties. Addition of diethylether to the reaction mixture leads to a heptanuclear mixed-metal cluster.

Results

Treatment of a solution of tris[(triphenylphosphine)gold(I)]sulfonium tetrafluoroborate [8] in dichloromethane with a solution of silver tetrafluoroborate (molar ratio of the reactants: 2:1) at 20 °C gives good yields (61%) of a colourless solid product upon precipitation by addition of diethylether to the reaction mixture. The compound is soluble in di- or trichloromethane, but insoluble in pentane or diethyl ether. The solid is stable to air and moisture, but the solutions undergo rapid decomposition.

The solutions of the product in CDC1₃ show one singlet signal in the ³¹P [¹H] NMR spectrum at 20 °C, indicating virtual equivalence of all ligands on the NMR time scale. Accordingly, the ¹H and ¹³C [¹H] spectra also have only one set of phenyl signals. These spectra also show the presence of a tetrahydrofuran solvate, which was later confirmed by elemental analysis and X-ray diffraction (below). The FD and FAB mass spectra exhibit the [S(AuL)₃]⁺ cation as the parent peak.

Crystals of compound 1 are monoclinic, space group C2/c, with Z = 4 formula units in the unit cell. The lattice is composed of independent trications and anions (ratio 1:3). The two tris[(triphenylophosphine)gold(I)]sulfonium components are related by a crystallographic center of inversion (Fig. 1). The silver atom is disordered over two positions which could be refined using a split model. The tetrahydrofuran is also distributed over two sites and was calculated as accompanying the silver atom in each of its two positions.

In both of the symmetry-related, equivalent positions the silver atom has close contacts to two sulfur atoms and three gold atoms, and is still susceptible to electrophilic attack by additional cations [LAu]⁺ or naked [Au]⁺. The products do not have sulfur-centered tetrahedral structures, but were found to be square pyramidal with distorted squares or rectangles of gold atoms. The short Au–Au edges of these units suggest stabilizing metal-metal bonding for these moieties and their aggregates [1,7].

In the present short note we report the addition of [Ag⁺⁺⁺ to [S(Au(Ph₃))₃]⁺⁺⁺ cations, which leads to a heptanuclear mixed-metal cluster.
Fig. 1. Structure of the trication of compound 1 with atomic numbering. The molecule has a crystallographic center of inversion. The silver atom and the tetrahydrofuran molecule are disordered over two positions related by the center of inversion. Only one setting is shown with the corresponding connectivities. (ORTEP, 50% probability ellipsoids, except for the phenyl groups; hydrogen atoms omitted.) Selected bond lengths [Å]: Ag-S 2.668(4), Ag-S’ 2.430(3), Ag-Au1 2.852(2), Ag-Au2 2.838(2), Ag-Au2’ 2.948(2), Au1-S 2.321(3), Au2-S 2.335(3), Au3-S 2.373(3), Au1-Au3 3.1097(7), Au2-Au2’ 3.0015(7), Ag-O 2.53(2).

is similar to that of the homometallic counterpart S\textsubscript{Au}$_4$ in the corresponding dications [7]. The two units are sharing the silver atom as a common vertex. The basic structure of the two S\textsubscript{Au}$_3$ pyramids is not changed significantly by the addition of the silver atom [8], and Au-Au distances between 3.0015(7) and 3.1097(7) Å are retained, which correspond to Au-S-Au angles as small as 79.21(9) – 82.97(9)°.

The tetrahydrofuran molecule shows the standard envelope conformation, and its oxygen atom has an O-Ag contact of 2.53(2) Å. The triphenylphosphine units show no anomalies. Further details of the structure determination and its results are summarized in the Experimental Part and have been deposited.

**Experimental Part**

All experiments were routinely carried out under dry, purified nitrogen. Standard equipment was used throughout. The sulfonium salt was prepared following published procedures [8].

**Preparation:** $[\text{S}(\text{AuPPh}_3)_3]^+$BF$_4^-$ (0.19 g, 0.13 mmol) is dissolved in CH$_2$Cl$_2$ (10 ml) and treated with a solution of AgBF$_4$ (0.013 g, 0.064 mmol) in C$_4$H$_8$O (2 ml) at 20 °C with stirring. After 1 h the solution is concentrated in a vacuum and layered with diethyl ether to precipitate the product. Colourless crystals are collected after 3 d (0.26 g, 61% yield).

C$_{108}$H$_{90}$AgAu$_6$B$_2$F$_{12}$P$_6$S$_2$, C$_4$H$_8$O (3260.05)
Calcld. C 41.26 H 3.03 Au 36.25 Ag 3.31%.
Found C 40.56 H 3.05 Au 36.00 Ag 3.30%.

MS (FD / FAB): m/z = 1408 (100%/35%), [S(AuPPh$_3$)$_3$]$^+$.

NMR (CDCl$_3$, 20 °C); $^{31}$P{'H}, d 33.04, s; $^1$H, 1.83 (m, CH$_2$, thf), 3.72 (m, CH$_2$, thf), 7.20–7.50 (m, Ph); $^{13}$C{'H}, 25.6 (s, CH$_2$, thf), 68.0 (s, CH$_2$, thf), 127.7 (d, J 60.1 Hz, Ph-C1), 129.6 (d, J 11.9 Hz, Ph-C3), 132.5 (s, Ph-C4), 133.8 (d, J 13.3 Hz, Ph-C2).

**Structure determination**

A specimen of suitable quality was mounted in a glass capillary and used for measurements of precise cell constants and intensity data collection. During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. Lp correction was applied and intensity data were corrected for absorption effects (psi-scans, µ(Mo-K$_\alpha$) = 80.50 cm$^{-1}$, $T_{min}/T_{max}$ = 0.672/1.000). The structure was solved by Patterson methods and completed by full-matrix least-squares techniques against F$^2$. All non-H atoms except for those of one disordered BF$_4$ anion and those of the solvent thf molecule were refined with anisotropic displacement parameters. All H-atoms were placed in idealized calculated positions and allowed to ride on their carbon atoms with $U_{iso}$(fix) = 1.5 x $U_{eq}$(C).

Crystal data: C$_{108}$H$_{90}$AgAu$_6$B$_2$F$_{12}$P$_6$S$_2$ x C$_4$H$_8$O, $M_r$ = 3259.94, colourless crystals of dimensions 0.1 x 0.13 x 0.6 mm, monoclinic, $a = 24.853(3)$, $b = 18.8982(2)$, $c = 24.347(3)$ Å, $\beta = 91.70(1)^\circ$, space group C2/c, Z = 4, $V = 11401.76$ Å$^3$, $D_{calc} = 1.901$ g cm$^{-3}$, $F(000) = 6176$; Enraf Nonius CAD4 diffractometer, Mo-K$_\alpha$ radiation ($\lambda = 0.71073$), $T = -62 ^\circ$C. From 9984 measured [(sin$\theta$/λ)$_{max}$ = 0.64 Å$^{-1}$] and 9769 unique reflections ($R_{int} = 0.028$) 7664 were used for refinement. The structure converged for 580 refined parameters to an $R$ (w$R^2$) value of 0.0532 (0.1299). Residual electron densities: +3.17/-2.72 eÅ$^{-3}$.

Further information on the X-ray structure determination can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 406335, the names of the authors, and the journal citation.