Synthesis of the Hexakis[(triphenylphosphane)gold(I)]methanium(2+) Cation from Trimethylsilyldiazomethane; Crystal Structure Determination of the Tetrafluoroborate Salt

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A new synthetic route to the bis(tetrafluoroborate) salt of the hexakis[(triphenylphosphane)gold(I)]methanium dication has been opened up through the reaction of trimethylsilyldiazomethane and tris[(triphenylphosphane)gold(I)]oxonium tetrafluoroborate in dichloromethane. Yields are close to 65% if the reaction is carried out in the presence of triethylamine as a base. The process is a sequence of desilylation, deprotonation and deazotation reactions at the carbon function of the diazomethane, as shown by the detection of intermediates. The crystal structure of the title compound (with three equivalents of crystal dichloromethane) has been determined in a single-crystal X-ray study. The dication has no crystallographically imposed symmetry, but the core is a distorted, carbon-centered octahedron of gold atoms. This result confirms the data from previous structural studies of salts with other anions and interstitial solvents.

Introduction

The discovery of hexaauriomethanium dications of the type $[(LAu)_6C]^{2+}$ ($L = PR_3$) in this laboratory in 1988[1] has attracted considerable attention, mainly because of the unusual hypercoordination of the central carbon atom in these novel species. The intriguing formula originally proposed for the dication has since been confirmed beyond reasonable doubt[2–6], and its electronic structure has been the subject of a number of quantum-chemical calculations[7–11]. The results of these theoretical studies are in agreement with experimental data and allow a satisfactory description of structure and bonding using highest level Hartree-Fock and Density-Functional models. Early predictions based on Extended Hückel Molecular Orbital methods were thus also confirmed[12]. The more recent calculations showed, however, that relativistic and correlation effects prove essential for a convincing reproduction of the structure and energy characteristics.

By contrast, the development of the *chemistry* of hexaauriomethanium salts $[(LAu)_6C]^{2+}\ 2\ X^-$ has proceeded much more slowly owing to the somewhat alchemistic methods for their preparation[1–6]. The original preparation was based on tetrakis(dialkoxyboryl)methane precursors $[(RO)_2B]_4C$ which are not readily available, required strict adherence to the published experimental procedure, and gave low yields. Various attempts to use other precursors, e.g. tetrasilyl/germyl/stannylmethanes instead of tetraborylmethanes, as substrates for auration reactions were unsuccessful.

As part of our continuing efforts, we recently investigated the auration reactions of trimethylsilyldiazomethane[13]. Treatment of Me_3SiCHN_2 with tris[(triphenylphosphane)-gold(I)]oxonium tetrafluoroborate $[(Ph_3P)Au]_3O^+BF_4^-$ was shown to give three products in low overall yield, of which two compounds were identified as 1) a conventional phosphonium salt $\{Ph_3PCH[Au(PPh_3)]_2\}^+\ BF_4^-$ (**1**) and 2) a novel tetraauriomethanium(+1) salt $\{HC[Au(PPh_3)]_4\}^+\ BF_4^-$ (**2**). The characterization of **1** and **2** included the determination of the crystal structure in both cases[13].

The third product has now finally been shown to be a hexaauriomethanium(+2) salt $\{[(Ph_3P)Au]_6C\}^{2+}\ 2\ BF_4^-$ (**3**). This observation gave the clue as to a new synthetic pathway towards the title compounds. The reaction could be optimized to give high yields of compound **3**, and the product was obtained as crystals suitable for X-ray diffraction studies. It should be noted that the cation contained in **3** has previously been structurally investigated only as the component of a salt with the rare $[F_3BOMe]^-$ anion found serendipitously as a methanolysis product.

In the present paper we summarize our new results, which can help to solve a few long-standing preparative and structural problems.

Preparative, Spectroscopic and Analytical Results

The reaction of equimolar quantities of Me_3SiCHN_2 and $[(Ph_3P)Au]_3O^+\ BF_4^-$ in tetrahydrofuran at −78 °C proceeds smoothly and leads to the concomitant formation of three gold-containing compounds, which can be separated by fractional crystallization (Experimental Section). As reported previously and mentioned in the Introduction[13], the first two fractions are readily identified as $\{Ph_3PCH[Au(PPh_3)]_2\}^+\ BF_4^-$ (colorless, 4% yield, **1**) and $\{HC[Au(PPh_3)]_4\}^+\ BF_4^-$ (yellow, 12% yield, **2**). Compound **2** appears (from dichloromethane/hexane) together with red needle-like crystals, which could be separated under a microscope (11% yield, **3**).

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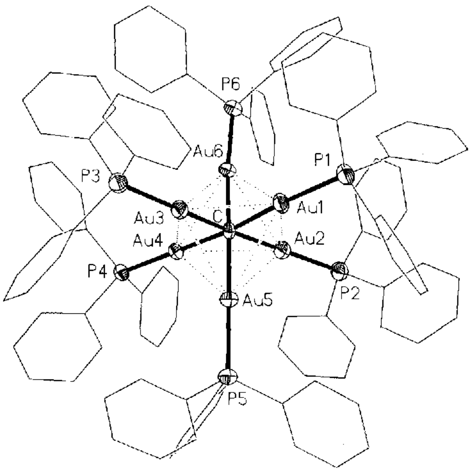
Figure 1. Structure of the dication of compound **3** with atomic numbering (ORTEP plot with 50% probability ellipsoids, H atoms omitted for clarity)[a]



[a] Selected bond lengths [Å]: Au1–Au2 2.887(1), Au1–Au3 2.928(1), Au1–Au5 3.194(1), Au1–Au6 3.057(1), Au2–Au4 3.226(1), Au2–Au5 2.913(1), Au2–Au6 2.936(1), Au3–Au4 2.941(1), Au3–Au5 3.038(1), Au3–Au6 3.132(1), Au4–Au5 2.908(1), Au4–Au6 2.896(1), Au1–C 2.12(1), Au2–C 2.13(1), Au3–C 2.09(1), Au4–C 2.14(1), Au5–C 2.11(1), Au6–C 2.15(1).

Yields of compound **3** are improved considerably (23%) if the same reaction is carried out in dichloromethane at room temperature and the product is precipitated directly by the addition of hexane. The preparation could finally be optimized further (64% yield) by adding stoichiometric quantities of triethylamine to the reaction mixture.

$Me_3SiCHN_2 + \{[(Ph_3P)Au]_3O\}^+ BF_4^- \rightarrow$

$\{Ph_3PCH[Au(PPh_3)]_2\}^+ BF_4^-$ (1)

$\{HC[Au(PPh_3)]_4\}^+ BF_4^-$ (2)

$\{[(Ph_3P)Au]_6C\}^{2+}\ 2\ BF_4^-$ (3)

The overall reaction can be interpreted as a multi-step desilylation, deprotonation and deazotation process, in which the carbon function of the Me_3SiCHN_2 is stripped of all its substituents and becomes coordinated to a maximum number of $[(Ph_3P)Au]^+$ cations. Triethylamine was added following the idea that deprotonation should be facilitated by a Brønsted base. The trimethylsilyl groups are transferred to the oxide anion introduced by the trigoldoxonium salt, and nitrogen is released as dinitrogen gas. Compound **2** is clearly an intermediate of this multi-step process, where the central carbon atom still carries the proton. Indeed, when **2** is allowed to react with $[(Ph_3P)Au]^+$, there is complete conversion to **3**. Some of the phosphane ligands can also be transferred from gold to carbon, as exemplified by compound **2**. Such a process is probably irreversible and accounts for the lowering of the yield. In the presence of Et_3N, this side reaction is also suppressed.

After drying in vacuo, compound **3** (m.p. 230 °C, dec.) was free of solvent and gave satisfactory elemental analysis data. Its FAB mass spectra showed the presence of the dication at *m/z* 1383.9 and of the monocation at *m/z* 2767.8. The ^{31}P-, ^{13}C- and ^{1}H-NMR parameters of the cation (for solutions in CD_2Cl_2) are identical to the data reported previously[1]. The ^{11}B- and ^{19}F-NMR data for the BF_4^- anions are in the range of literature values, but different from those of the $[F_3BOMe]^-$ anion present in previous samples[1]. The standard NMR chemical shifts and line widths observed confirm that compound **3** is diamagnetic.

Structural Results

Crystals of compound **3** as obtained from dichloromethane/hexane at −25 °C contain three equivalents of dichloromethane. The crystals are monoclinic, space group $P2_1/c$, with four formula units in the unit cell. The lattice is built up of independent dications and anions with no unusual sub-van der Waals contacts between these components or between the ions and the solvent molecules. One of the anions was found to be disordered, but the arrangement could be accounted for by a split-atom model (below).

The structure of the dication is shown in Figure 1. Contrary to the situation in the $[F_3BOMe]^-$ salt investigated previously[1], where the central carbon atom is residing on a center of inversion, in the new phase ($3 \times 3\ CH_2Cl_2$) it has no crystallographically imposed symmetry. The gold atoms form a distorted octahedron with Au–Au edges in the range 2.887(1)–3.226(1) Å and Au–C distances between 2.09(1) and 2.15(1) Å. The coordination geometry at each gold atom is close to linear, with Au–P distances between and 2.254(4) and 2.277(4) Å and C–Au–P angles between 172.3(4) and 178.9(4)°. All Au–C–Au angles are close to 90 or 180 °C. The geometries of the six triphenylphosphane units show no anomalies.

When compared with previously determined parameters for the F_3BOMe salt[1], the Au–Au edges and Au–C and Au–P bonds are found to be in the same ranges [2.910(1)–3.053(1) Å; 2.122(2)–2.129(2) Å; 2.269(1)–2.274(1) Å, respectively], thus corroborating these and other documented data[2–6].

Not surprisingly, the dimensions of species with chelating large-bite bis(diarylphosphane) ligands[3] or with bulkier tri*alkyl*phosphanes[4] show more severe distortions depending on ligand requirements, but the fundamentals of the structures are the same.

Conclusions

This work has demonstrated that hexaauriomethanium salts are readily accessible from convenient starting materials and under conventional laboratory conditions. The products are now available in larger quantities for the further pursuit of their chemistry.

The structural studies of the bis(tetrafluoroborate) tris(dichloromethane) phase confirmed the proposed structure, but the CAu_6P_6 core again shows significant distortions from a regular octahedron, well beyond the standard deviations of the experiment. This may indicate that there is a perference for a few very short Au···Au contacts on the expense of other Au···Au interactions along neighboring octahedral edges. Such distortions are not uncommon in the structural chemistry of gold clusters with interstitial atoms[6]. For the present case it appears that carbon is not a perfect match for the interstice in an octahedron of gold atoms.

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Experimental Section

General: All experiments were carried out under dry, purified N_2. Glassware was dried and filled with N_2; solvents were dried, distilled and kept under N_2. – NMR: Jeol GX 400; TMS and a 85% H_3PO_4 aqueous solution were used as external standards for ^1H and ^{31}P NMR, respectively. – MS: Finnigan MAT 90. – Microanalyses: In-house analyzers (by combustion). – Trimethylsilyldiazomethane was purchased from Aldrich Chemicals as a 2 M hexane solution and was used without further purification. Triethylamine was dried and distilled from CaH_2. The oxonium salt $[(Ph_3P)Au]_3O^+$ BF_4^- was prepared according to a literature procedure[14].

Reaction of Me_3SiCHN_2 with $[(Ph_3P)Au]_3O^+$ BF_4^- in THF: To a slurry of $[(Ph_3P)Au]_3O^+$ BF_4^- (500 mg, 0.34 mmol) in THF (8 ml) cooled to −78 °C was added a 2 M hexane solution of Me_3SiCHN_2 (0.25 ml, 0.5 mmol). The resulting mixture was allowed to warm to 25 °C and was stirred for another 3 h during which time the solution became red and a precipitate formed. The THF solution was decanted and the solvent evaporated. The resulting residue was dissolved in CH_2Cl_2 and a layer of hexane was allowed to diffuse into the resulting solution which resulted in the crystallization of 24 mg of compound **1** (4% yield based on gold)[13]. The THF-insoluble pecipitate was dissolved in CH_2Cl_2 and layered with hexane which led to the formation of two types of crystals which could be separated on the basis of their morphology and color. Yellow, chunky crystals of the previously reported compound **2** were formed in a 12% yield based on gold[13]. Red, needle-like crystals of **3** were formed in an 11% yield based on gold (60 mg, m.p. 230 °C, dec.). – $C_{109}H_{90}Au_6B_2F_8P_6$ (2941.25): calcd. C 44.45, H 3.06, Au 40.2; found C 44.22, H 3.10, Au 40.2.

Reaction of Me_3SiCHN_2 with $[(Ph_3P)Au]_3O^+$ BF_4^- in CH_2Cl_2: To a solution of $[(Ph_3P)Au]_3O^+$ BF_4^- (450 mg, 0.30 mmol) in CH_2Cl_2 (5 ml) was added a 2 M hexane solution of Me_3SiCHN_2 (0.2 ml, 0.4 mmol). The resulting mixture was stirred for 3 h during which time the color turned to red. A layer of hexane (5 ml) was then allowed to diffuse into the solution which resulted in the crystallization of 100 mg of compound **3** (23% yield based on gold).

Reaction of Me_3SiCHN_2 with $[(Ph_3P)Au]_3O^+$ BF_4^- in CH_2Cl_2 in the presence of Et_3N: To a solution of $[(Ph_3P)Au]_3O^+$ BF_4^- (240 mg, 0.16 mmol) in CH_2Cl_2 (3 ml) were added Et_3N (0.02 ml, 0.16 mmol) and a 2 M hexane solution of Me_3SiCHN_2 (0.08 ml, 0.16 mmol). The resulting mixture was stirred for 3 h during which time the color turned to red. A layer of hexane (5 ml) was then allowed to diffuse into the solution which resulted in the crystallization of 150 mg of compound **3** (64% yield based on gold).

Crystallographic Structure Determination: A maybe somewhat too large specimen (0.4 × 0.23 × 0.2 mm) was mounted in a glass capillary and used for measurements of precise cell constants and intensity-data collection. Diffraction measurements were made with an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with ω-scan mode at −68 °C. Lp correction was applied and intensity data were corrected for decay (−5.6%) and absorption effects (ψ scans, T_{min}/T_{max} = 0.69/0.99). The structure was solved by direct methods and completed by full-matrix least-squares refinement in three blocks against F (SHELXTL-PLUS). – $C_{112}H_{96}Au_6B_2Cl_6F_8P_6$; M_r = 3195.99; monoclinic; a = 27.454(2), b = 17.715(1), c = 25.164(2) Å; β = 93.39(1)°; space group $P2_1/c$ (No. 14); Z = 4, $D_{calcd.}$ = 1.959 g cm^{-3}; $F(000)$ = 6064 e; μ(Mo-K_α) = 83.6 cm^{-1}. 22456 intensity data were measured up to $(\sin\Theta/\lambda)_{max}$ = 0.59 Å^{-1}, of which 13503 independent structure factors were considered "observed" $[F_o \geqslant 5\sigma(F_o)]$ and used for refinement. The non-H atoms of the dication were refined with anisotropic displacement parameters; due to disorder, the BF_4^- anions and the three solvent CH_2Cl_2 molecules were treated isotropically. H atoms of the dication were placed in idealized calculated positions and allowed to ride on their carbon atoms. The function minimized was $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. The final R and R_w values were 0.0526 and 0.0567, respectively, for 1182 refined parameters; residual electron densities: +6.43/−2.29 eÅ^{-3}, located around gold atoms. Further information on the X-ray structure determination can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-405831.

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[1] F. Scherbaum, B. Grohmann, B. Huber, C. Krüger, H. Schmidbaur, *Angew. Chem.* **1988**, *100*, 1602; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1544.

[2] O. Steigelmann, P. Bissinger, H. Schmidbaur, *Angew. Chem.* **1990**, *102*, 1473; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1399.

[3] H. Schmidbaur, B. Brachthäuser, O. Steigelmann, *Angew. Chem.* **1991**, *103*, 1552; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1488.

[4] H. Schmidbaur, B. Brachthäuser, O. Steigelmann, H. Beruda, *Chem. Ber.* **1992**, *125*, 2705.

[5] H. Schmidbaur, B. Brachthäuser, S. Gamper, A. Schier, O. Steigelmann, *Z. Naturforsch.* **1992**, *47b*, 1725.

[6] H. Schmidbaur, *Chem. Soc. Rev.* **1995**, 391.

[7] N. Rösch, A. Görling, D. E. Ellis, H. Schmidbaur, *Angew. Chem.* **1989**, *101*, 1410; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1357.

[8] A. Görling, N. Rösch, D. E. Ellis, H. Schmidbaur, *Inorg. Chem.* **1991**, *30*, 3986.

[9] P. Pyykkö, Y. Zhao, *Chem. Phys. Lett.* **1991**, *117*, 103.

[10] K. Burdett, O. Eisenstein, W. B. Schweizer, *Inorg. Chem.* **1994**, *33*, 3261.

[11] O. D. Häberlen, H. Schmidbaur, N. Rösch, *J. Am. Chem. Soc.* **1994**, *116*, 8241.

[12] D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.* **1976**, 1163.

[13] H. Schmidbaur, F. P. Gabbaï, A. Schier, J. Riede, *Organometallics* **1995**, *14*, 4969.

[14] N. Nesmeyanov, E. G. Perevalova, Yu. T. Struchkov, M. Yu. Antipin, K. I. Grandberg, V. P. Dyadchenko, *J. Organomet. Chem.* **1980**, *201*, 343.

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