

Polygold(1-adamantyl)ammonium Salts

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The reaction of 1-adamantylamine with tris(triphenylphosphaneaurio)oxonium tetrafluoroborate results in the formation of the trinuclear adamantyltris(triphenylphosphaneaurio)ammonium tetrafluoroborate $[C_{10}H_{15}N[Au(PPh_3)_3]^+ BF_4^-]$. The product can be further aurated by addition of equimolar

amounts of triphenylphosphaneaurio tetrafluoroborate to give the tetranuclear complex $\{C_{10}H_{15}N[Au(PPh_3)_3]_4\}^{2+} \{BF_4^-\}_2$. Both compounds have been fully characterized by analytical and spectroscopic data, and in the case of the trinuclear complex by a single crystal X-ray structure determination.

Introduction

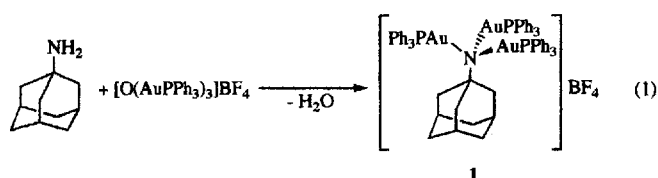
After a slow development in the previous decades, the chemistry of gold-nitrogen compounds has recently been extensively studied. This is particularly true for compounds in which nitrogen atoms act as nucleation centres for gold clustering^[1–16]. In the course of these investigations it has been demonstrated that the stability of the gold-nitrogen clusters increases as the number of gold atoms rises^[17]. Strongly aurating agents like $[AuL]^+X^-$ or $[(AuL)_3O]^+X^-$ (L = tertiary phosphane, X = noncoordinating counterion) can aurate the nitrogen atom of ammonia to give not only quaternary ammonium salts of the type $[(AuL)_4N]^+[1,2,10,16]$, but also hypercoordinate species like $[(AuL)_5N]^{2+}[18]$, in much the same way as exhaustive auration of methane leads to the formation of $[(AuL)_4C]$ and the hypercoordinate species $[(AuL)_5C]^+$ and even $[(AuL)_6C]^{2+}$, with tetrahedral, trigonal bipyramidal and octahedral structures, respectively^[18].

In the carbon series, partially alkylated centroid atoms lead to molecules or cations of the type $[(AuL)_3CR]$ or $[(AuL)_4CR]^+$ with tetrahedral or square-pyramidal structures, respectively^[19]. In much the same way primary amines have been shown to afford ammonium salts $[(AuL)_3NR]^+[15]$, but the exhaustive auration of these amines was found to lead to $[(AuL)_4N]^+$ salts by dealkylation with N–C cleavage. In an attempt to preserve the C–N bond and thus allow the build-up of dications $[(AuL)_4NR]^{2+}$ with pentacoordinate nitrogen atoms, primary amines RNH_2 where R has poor leaving group properties, like the 1-adamantyl case, have now been investigated.

Results and Discussion

The reaction of 1-adamantylamine with tris(triphenylphosphaneaurio)oxonium tetrafluoroborate, $[(AuPPh_3)_3O]^+BF_4^-$ ^[1,2], in dichloromethane results in the formation of 1-adamantyltris(triphenylphosphaneaurio)ammonium

tetrafluoroborate as a stable colourless solid in high yields (80%) (equation 1).



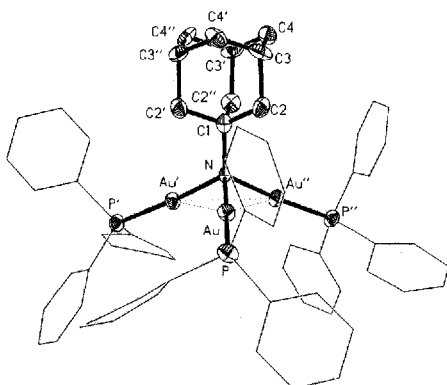
The composition of the product is readily confirmed by elemental analysis and field-desorption mass spectrometry [$m/z = 1526.1$ (100%) for the cation]. The ¹H-NMR spectrum of a solution in CDCl₃ shows multiplet resonances at $\delta = 1.2$ – 2.3 (m) (CH, CH₂; 15H) for the adamantyl group and at $\delta = 7.2$ – 7.6 (m) (C₆H₅; 45H) for the phenyl groups. The ³¹P{¹H}-NMR spectrum in the same solvent, exhibits the expected singlet resonance at $\delta = 29.5$.

Only a few single crystals suitable for an X-ray study were obtained when the reaction mixture in dichloromethane was layered with diethyl ether at room temperature. Rather surprisingly, the resulting crystals contained, in addition to the expected trinuclear gold cation and the BF₄⁻ anion, one molecule of Ph₃P–Au–Cl. This phosphane gold chloride, which probably originates from residual starting material in the gold(I)oxonium salt, was absent in the bulk product isolated from the mother liquor after reducing the volume and subsequent precipitation with diethyl ether (see above and the Experimental Section).

The crystals are hexagonal, space group $P6_3$, with two formula units in the unit cell. The lattice is built up of independent monomeric complex cations and anions, and no unusual sub-van der Waals contacts are observed between these components or between the ions and the Ph₃P–Au–Cl molecule. The structure of the cation is shown in Figure 1.

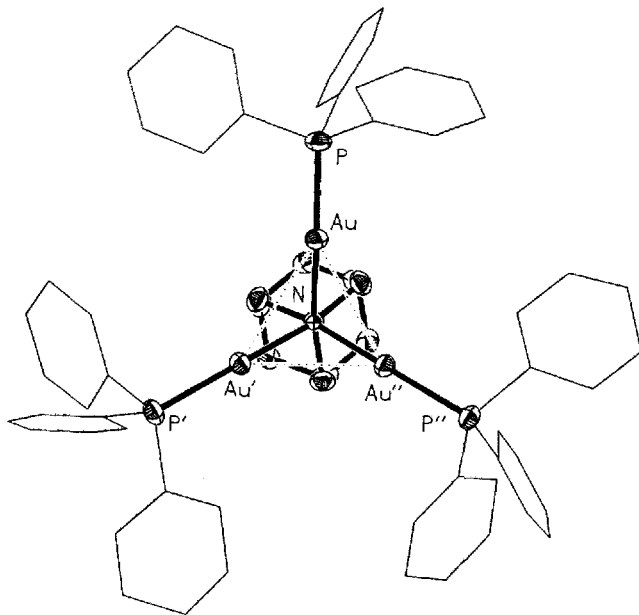
It has a crystallographically imposed threefold axis (N–C1) relating the three gold atoms attached to the nitrogen atom. In the pyramidal N Au₃ unit the three equivalent

Figure 1. Structure of the cation of compound **1** with atomic numbering (ORTEP plot with 50% probability ellipsoids, H atoms omitted for clarity); selected bond lengths [Å] and angles [°]: Au...Au' 3.202(1); Au–N 2.043(6), Au–P 2.255(3), N–C1 1.53(3), N–Au–P 176.2(4); C1–N–Au 115.2(4)

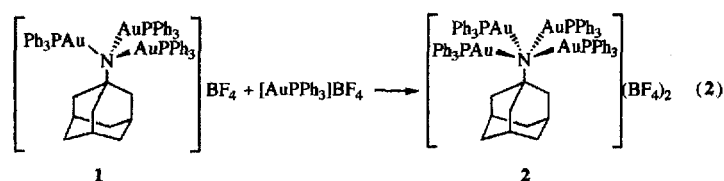


angles Au–N–Au' of only 103.2(5)° are associated with short contacts between the gold centres of 3.202(1) Å. The angles N–Au–P of 176.2(4)° are close to the ideal value for a linear geometry. The adamantyl group is in a staggered orientation relative to the NAu₃ pyramid (Figure 2). The Ph₃P–Au–Cl molecule also has crystallographic threefold symmetry. Its structural details are very similar to the averaged parameters determined for the pure phase, which has no crystallographic symmetry^[20]. Treatment of compound **1** with a further equivalent of [triphenylphosphane]gold(I) tetrafluoroborate gave a pale-yellow solid, which is assigned the structure of a square-pyramidal tetranuclear complex on the basis of analytical and spectroscopic data (equation 2).

Figure 2. Structure of the cation of compound **1**, viewed along the threefold axis and showing the staggered orientation of the adamantyl group relative to the NAu₃ pyramid



The field desorption mass spectrum shows the parent ion at $m/z = 993.5$ (7%) and peaks corresponding to the loss of



one [$m/z = 1526.1$ (93.7%)] and two [$m/z = 1068.2$ (100%)] AuPPh₃ groups. The ¹H-NMR spectrum in CDCl₃ exhibits resonances of the adamantyl and phenyl groups at $\delta = 1.51$ – 2.26 (m) (CH, CH₂; 15H) and 7.4 – 7.6 (m) (C₆H₅; 60H), respectively, and the ³¹P{¹H} spectrum features a singlet at $\delta = 31.0$ (s). There are no significant changes as the probe temperature is lowered to -50°C . All data are distinctly different from those of the precursor **1**, and the intensity ratio of alkyl vs. aryl resonances is particularly diagnostic. Unfortunately no single crystals could be grown of compound **2**, and therefore the square-pyramidal structure expected on the basis of reference data for [RC(AuL)₄]⁺ cations^[19] must remain unconfirmed.

The tetranuclear species [AdN(AuL)₄]²⁺ is unprecedented, except for a case where a pyridine function of a quinolinyl group was allowed to assist the assembling of the tetranuclear unit at the neighbouring amino group^[12]. In the dication {(C₉H₆N)N[Au(PPh₃)₄]}²⁺ the four gold atoms are found to form a rectangle capped by the two nitrogen atoms of the 8-aminoquinoline ligand. An analogous structure is proposed for the dication of compound **2**. Steric effects and poor leaving-group properties of the adamantyl group appear to be instrumental in keeping the N–C bond intact, since all experiments with R = Me, Et, *i*Pr, *t*Bu failed to give analogous products and led to C–N cleavage with formation of N(AuL)₄⁺ or N(AuL)₃²⁺ clusters^[5,7,8].

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Experimental Section

Synthesis of Complex 1: To a solution of 1-adamantylamine (0.015 g, 0.10 mmol) in 20 ml of dichloromethane under nitrogen was added [O(AuPPh₃)₃]BF₄ (0.150 g, 0.10 mmol). After 2 h the solvent was concentrated to ca. 3 ml. Addition of diethyl ether afforded complex **1** as a white solid. Yield 0.13 g, 80%. – C₆₄H₆₀Au₃BF₄NP₃ (1613.8): calcd. C 47.60, H 3.75, N 0.80; found C 47.03, H 3.79, N 0.70%.

Synthesis of Complex 2: To a freshly prepared solution of [AuPPh₃]BF₄ (0.06 mmol) in THF kept at 0°C was added compound **1** (0.100 g, 0.06 mmol). The resulting yellow solution was stirred for 1 h and the solvent was removed in vacuum. After addition of diethyl ether complex **2** was obtained as a pale-yellow solid. Yield 0.08 g, 65%. – C₈₂H₇₅Au₄B₂F₈NP₄ (2159.89): calcd. C 45.60, H 3.50, N 0.65; found C 45.31, H 3.48, N 0.60%.

Crystal Structure Determination: A suitable crystal of **1** · Ph₃P–Au–Cl 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. No significant changes were observed. Diffraction intensities were corrected for L_p and absorption effects. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atom. Important interatomic distances and angles are summarized in the figure caption. Anisotropic thermal parameters, and tables of interatomic distances and angles are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen on quoting the depository number CSD-406144.

Crystal Data: $C_{82}H_{75}Au_4BClF_4NP_4$, $M_r = 2108.44$, colourless crystal of dimensions $0.3 \times 0.5 \times 0.5$ mm, hexagonal, $a, b = 15.624(1)$, $c = 17.863(1)$ Å, space group $P6_3$, $Z = 2$, $V = 3776.3(4)$ Å³, $D_{calc} = 1.854$ g cm⁻³, $F(000) = 2016$; Enraf Nonius CAD4 diffractometer, Mo- K_α radiation ($\lambda = 0.71073$ Å), $T = -68^\circ\text{C}$; $\mu(\text{Mo-}K_\alpha) = 79.2$ cm⁻¹, psi-scans, $T_{min/max} = 0.90/0.99$. Solution with Patterson methods using SHELXTL-PLUS. From 5736 measured $[(\sin\Theta/\lambda)_{max} = 0.62 \text{ Å}^{-1}]$ reflections 5154 were used for refinement against $F^2(\text{SHELXL-93})$. The structure converged for 291 refined parameters to an $R1$ ($wR2$) value of 0.0477 (0.1272). Flack parameter: 0.05(2); GOF: 1.002. The function minimized was $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$, $w = 1/\sigma^2(F_o^2) + (ap)^2 + bp$, with $p = (F_o^2 + 2F_c^2)/3$, and $a = 0.0844$ and $b = 34.28$. Residual electron densities: $+1.72/-4.15 \text{ eÅ}^{-3}$, located around the gold atom of the $\text{Ph}_3\text{P-Au-Cl}$ moiety.

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