# Further Gold Aggregation at a Pentanuclear Gold Cluster with Hypercoordinate Interstitial Nitrogen

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Cationic complexes of univalent gold of the type $[LAu]^+$, with L as an electron-pair donor ligand, have been classified as isolobal[1,2] with the corresponding derivatives of the proton $[H]^+$ and the carbonium ions $[R]^+$. The stoichiometry of reactions, and the structural chemistry of such seemingly unrelated systems, support this concept, which has proved exceedingly useful as a heuristic principle.[3] Thus the classical hydronium ion $[H_3O]^+$, the cations of Meerwein's salts[4] $[R_3O]^+$, and Nesmeyanov's tris(gold)oxonium cations[5] $[(LAu)_3O]^+$ may be mapped isolobally.

For the related nitrogen system, there is also the analogy for $[NH_4]^+$, $[NR_4]^+$, and $[(LAu)_4N]^+$, but, surprisingly, with $[LAu]^+$ a pentacoordinate species $[(LAu)_5N]^{2+}$ has also been discovered[6] (eq 1), for which there is no parallel with the

$$[(Ph_3PAu)_4N]\,BF_4 \xrightarrow{(Ph_3PAu)\,BF_4} [(Ph_3PAu)_5N](BF_4)_2 \quad (1)$$

isolobal proton or carbonium ions: Dications $[NH_5]^{2+}$ and $[NR_5]^{2+}$ have never been observed, and according to theoretical calculations these species should in fact not be stable.[7,8]

The stability of the pentagold dication $[(LAu)_5N]^{2+}$ has been tentatively ascribed[9] to significant peripheral gold–gold interactions in the trigonal-bipyramidal $Au_5N$ core, and theoretical studies, including relativistic effects, support this idea, relating it mainly to correlation effects.[9–11]

To date, the experimental and theoretical studies have relied on only one example of the species $[(LAu)_5N]^{2+}$, with L = $PPh_3$ (and $BF_4^-$ as the counterion). Nevertheless the species has been fully characterized by analytical, spectroscopic and structural data.[6] Work on other members of the series, e.g. with different ligands L and/or different counterions, was therefore highly desirable. Recent studies along these lines were initially unsuccessful, however, and only with the system with L = $PMe_3$ could some progress be made, as described in this report.

## Results

Auration of ammonia with the reagent[12] $[(Me_3PAu)_3O]^+BF_4^-$ in dichloromethane at low temperature (−25 °C) gives a series of partially aurated ammonium salts depending on the stoichiometry of the reagents.[13] With the appropriate quantity of the oxonium salt, a colorless solid can be isolated which is readily characterized as the expected $[(Me_3PAu)_4N]^+BF_4^-$ salt by its analytical, NMR spectroscopic and mass spectrometric data.[13] Although there is no direct evidence, a tetrahedral structure can be tentatively assigned to the cation, but with severe distortions as previously observed for the homologues.[14–17] The reasons for these structural irregularities have been discussed.[17]

Instead of ammonia, hexamethyldisilazane can also be used as a starting material for the auration reactions. Primary products of a treatment with the oxonium salt $[(Me_3PAu)_3O]^+[BF_4]^-$ are partially silylated ammonium salts,[13] mainly $[(Me_3PAu)_3NSiMe_3]^+[BF_4]^-$. Further reaction with the oxonium salt in the presence of $Me_3PAuCl$ affords a colorless crystalline product, which has now been identified as the {pentakis[(trimethylphosphine)gold(I)]ammonio(2+)}bis[chloro(trimethylphosphine)gold(I)] bis[tetrafluoroborate(1−)], (**1**) with the formula $\{[(Me_3PAu)_5N][Me_3PAuCl]_2\}^{2+}[BF_4^-]_2$.

$$HN(SiMe_3)_2 \xrightarrow{[(Me_3PAu)_3O]\,BF_4} [(Me_3PAu)_3NSiMe_3]\,BF_4 \xrightarrow{[(Me_3PAu)_3O]\,BF_4} [(Me_3PAu)_5N](BF_4)_2 \xrightarrow{(Me_3PAu)Cl} [(Me_3PAu)_5N](BF_4)_2{\cdot}2(Me_3PAuCl) \quad (2)$$

Observations by a series of control experiments[13] suggest that the penta(gold)ammonium salt $[(Me_3PAu)_5N]^{2+}(BF_4^-)_2$ itself is rather labile, and that it is only with the aid of $Me_3PAuCl$ that a crystalline material stable at room temperature can be obtained. This ($Me_3PAuCl$) "ligand" is available in the reaction mixture owing to incomplete metathesis with $Ag_2O$ in the preparation of the oxonium salt.[12] Deliberate addition of $Me_3PAuCl$ could be shown to improve the yield (ca. 65%) of the serendipitously encountered product as colorless crystals (mp 145 °C with decomposition, from dichloromethane).

The composition of the product was confirmed by elemental analysis. Field desorption mass spectra show the complete dication (inclusive of the two $Me_3PAuCl$ molecules) as the parent peak (100%) and the dication $[(Me_3PAu)_5N]^{2+}$ (8% intensity). Solutions in chloroform at ambient temperature show two singlet resonances in the $^{31}P$ NMR spectra at $\delta = -10.0$ and $-15.0$ ppm with relative intensities of 2:5.

Single crystals of compound **1** (monoclinic, space group $P2_1/c$, $Z = 4$) are obtained from solutions of the product mixtures in dichloromethane. The lattice is composed of independent

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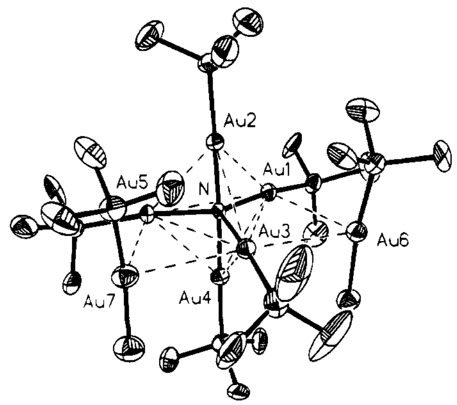


**Figure 1.** Structure of the dication $\{[(Me_3PAu)_5N][Me_3PAuCl]_2\}^{2+}$ in the lattice of the tetrafluoroborate salt **1** (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). For selected bond lengths and angles see Table 1.

**Table 1.** Comparison of Selected Distances (pm) and Angles (deg) of $[(Me_3PAu)_5N]^{2+}$ and $[(Ph_3PAu)_5N]^{2+}$

| | $[(Me_3PAu)_5N]^{2+}$ | $[(Ph_3PAu)_5N]^{2+}$ |
|---|---|---|
| $N-Au_{eq}$ | 207(2) | 205.1(7) |
| | 207(2) | 206.6(7) |
| | 209(2) | 208.1(6) |
| $N-Au_{ax}$ | 209(2) | 211.2(6) |
| | 216(2) | 211.6(6) |
| $Au_{eq}-N-Au_{eq}$ | 114.8(8) | 109.6(3) |
| | 117.9(8) | 121.4(3) |
| | 124.7(8) | 129.0(3) |
| $Au_{ax}-N-Au_{ax}$ | 173.7(9) | 174.9(4) |

tetrafluoroborate anions and a large composite cluster dication with no crystallographically imposed symmetry (Figure 1). As indicated above the latter can be recognized as an adduct of two molecules of $Me_3PAuCl$ and the dication $[(Me_3PAu)_5N]^{2+}$. Regarding the geometry of the $(PAu)_5N$ core, the structure of the dicationic unit is remarkably similar to the geometry of the phenyl homologue (Table 1).[6] Two apical Au atoms (Au2, Au4) are readily distinguished from the three equatorial Au atoms (Au1, Au3, Au5) at the trigonal bipyramidal (tbp) nitrogen center, with Au−N−Au angles close to 90 or 120°, respectively. Two of the three equatorial edges of the tbp core (Au1−Au3 and Au3−Au5) are bridged by the gold atoms (Au6 and Au7, respectively) of the two $Me_3PAuCl$ molecules. The equatorial plane thus contains five gold atoms at the vertices of three edge-sharing, almost equilateral triangles, thus forming a trapezoid geometry (Figure 2). The Au−Au contacts are in the usual range well established for auriophilic bonding (Table 2).[6,12,18]

The geometry of the two $Me_3PAuCl$ molecules is bent at the Au atoms in such a way that closer Au−Au contacts with the dication are possible. A similar bending is observed for the P−Au−N angles of the dication. The equatorial gold contact atoms are drawn together to give smaller angles Au1−N−Au3 [114.8(8)°] and Au3−N−Au5 [117.9(8)°], but a larger angle Au1−N−Au5 [124.7(8)°] on the nonbridged side.

The orientation of the two host molecules ($Me_3PAuCl$) is head to head (both phosphines on the same side of the equatorial plane) and roughly parallel to the $\psi$-$C_3$ axis of the tbp core. The resulting steric crowding also gives rise to slight distortions of the $(PAu)_5N$ core, with the sum of the equatorial angles at nitrogen reduced from 360 to 357.4°, and the Au2−N−Au4 axis bent from 180 to 173.7(9)°. The seven $Me_3P$ ligands are rotated into positions of minimum repulsion.

It is interesting to note that the structure of the dication of compound **1** is clearly related to the hexanuclear dication

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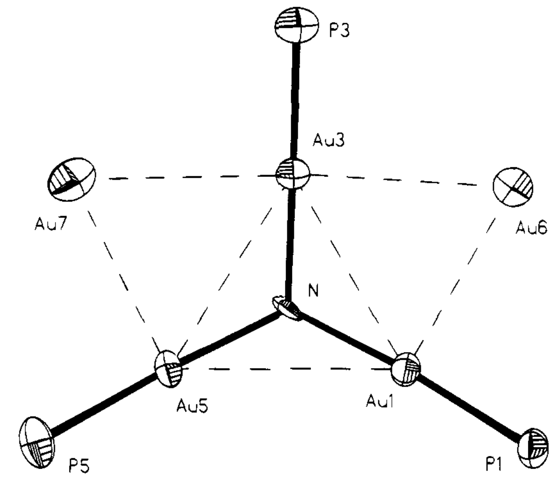



**Figure 2.** Section of the dication in compound **1** representing the plane of the equatorial gold atoms (Au1, Au3, Au5) of the trigonal bipyramidal core (Figure 1) together with the gold atoms Au6 and Au7 of the $Me_3PAuCl$ molecules.

**Table 2.** Selected Distances (pm) and Angles (deg) for $[(Me_3PAu)_5N](BF_4)_2{\cdot}2(Me_3PAuCl)$, **1**

| | | | |
|---|---|---|---|
| Au1−N | 207(2) | Au2−N−Au4 | 173.7(9) |
| Au2−N | 209(2) | Au1−N−Au3 | 114.8(8) |
| Au3−N | 209(2) | Au1−N−Au5 | 124.7(8) |
| Au4−N | 216(2) | Au3−N−Au5 | 117.9(8) |
| Au5−N | 207(2) | Au2−N−Au1 | 92.7(7) |
| Au2−Au1 | 301.3(1) | Au2−N−Au3 | 100.6(7) |
| Au2−Au3 | 321.9(1) | Au2−N−Au5 | 93.1(7) |
| Au2−Au5 | 301.8(1) | Au4−N−Au1 | 84.6(6) |
| Au4−Au1 | 285.1(1) | Au4−N−Au3 | 85.6(6) |
| Au4−Au3 | 289.3(1) | Au4−N−Au5 | 83.8(6) |
| Au4−Au5 | 282.6(1) | Au1−Au6−Au3 | 63.9(1) |
| Au6−Au1 | 325.2(1) | Au3−Au7−Au5 | 64.7(1) |
| Au6−Au3 | 337.8(2) | Au6−Au1−N | 92.5(4) |
| Au7−Au3 | 338.2(2) | Au6−Au3−N | 88.6(5) |
| Au7−Au5 | 328.2(2) | Au7−Au3−N | 87.0(5) |
| Au1−Au3 | 351.1(1) | Au7−Au5−N | 90.1(4) |
| Au1−Au5 | 367.0(1) | Au1−Au3−Au5 | 62.5 |
| Au3−Au5 | 356.7(1) | Au3−Au1−Au5 | 59.5 |
| | | Au1−Au5−Au3 | 58.0 |

$\{[(Me_3PAu)_3O]_2\}^{2+}$, in which a central gold *tetrahedron* has two opposite edges bridged by additional gold atoms [12] (Figure 3a). In the present case, the central pentanuclear *trigonal bipyramid* is transformed into a larger aggregate by the bridging of two equatorial edges (Figure 3b). This structure raises the question why no further addition of $Me_3PAuCl$ molecules takes place, e.g. to form a third bridge between atoms Au1 and Au5 thus completing the trapezoid to give a large $Au_6$ triangle (Figure 2). It appears that the distortions induced by the first two additions (above) are such, that the widening of the Au1−N−Au5 angle makes any further additions unfavorable.

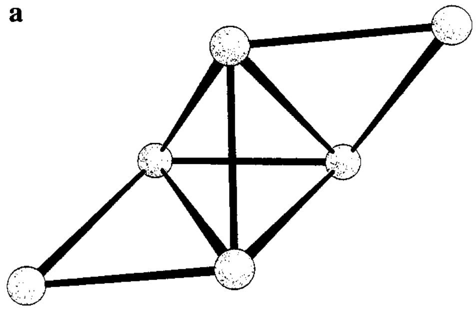
## Discussion

The results of this work are meaningful on three grounds: (1) A second example of a pentanuclear gold cluster with hypercoordinate nitrogen of the type $[(LAu)_5N]^{2+}$ has been prepared and characterized, which confirms the previous findings on an isolated case with $Ph_3P$ ligands,[6] as compared to $Me_3P$ ligands in the present case.

(2) For the first time, the gold atoms of a polynuclear gold cluster with hypercoordinate interstitial atoms have been shown to exhibit auriophilic bonding with molecular gold(I) complexes to give a poly-deltahedral aggregate of gold atoms.

(3) The structure of this aggregate shows all the geometrical details expected for supramolecular interactions based on intra-

a



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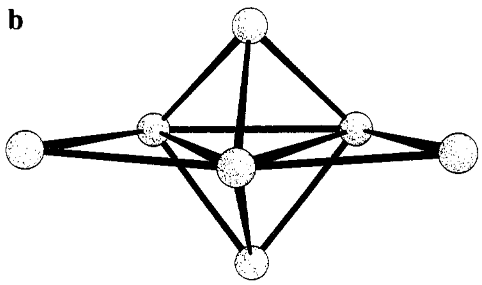

**Figure 3.** Arrangement of the gold atoms in the dication (a) of $\{[(Me_3PAu)_3O]_2\}^{2+}$ [12] and (b) of compound **1**.

and intermolecular bonding between seemingly closed-shell metal centers. This observation is indicative of an even broader scope of auriophilicity-based supramolecular chemistry.[18]

## Experimental Section

**General Data.** Experimental techniques required for work as described in this paper have been outlined in previous reports.[12,13]

**{Pentakis[(trimethylphosphine)gold(I)]ammonio(2+)bis[chloro(trimethylphosphine)gold(I)](*Au–Au*) bis(tetrafluoroborate) (1).** A solution of hexamethyldisilazane (40 mg, 0.24 mmol) in dichloromethane (5 mL) is added slowly to a solution of tris[(trimethylphosphine)gold(I)]oxonium tetrafluoroborate (246 mg, 0.27 mmol) and chloro(trimethylphosphine)gold(I) (34.0 mg, 0.11 mmol) in $CH_2Cl_2$ (25 mL) at ambient temperature. The reaction mixture is stirred for 24 h at 20 °C. After the volume is reduced to 10 mL in a vacuum, diethyl ether is added to precipitate the products, which are purified by recrystallization from a small volume of dichloromethane (colorless crystals, 48% yield, dec temp. 145 °C). MS (FD): m/z = 997 (100%); 680 (8%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = -10.0$ ppm (s, 2P, PAuCl), −15.0 (s, 5P, PAuN). Anal. Calcd for $C_{21}H_{63}Au_7Cl_2NP_7B_2F_8$ (2169.79): C, 11.62; H, 2.88; N, 0.64. Found: C, 11.27; H, 2.45; N, 0.5.

Crystal and structure solution data for $C_{21}H_{63}Au_7Cl_2NP_7B_2F_8$, **1**: $M_r$ = 2169.79, monoclinic, $a$ = 18.063(2) Å, $b$ = 11.337(1) Å, $c$ = 24.808(5) Å, $\beta$ = 95.96(1)°, space group $P2_1/c$ (No. 14), $V$ = 5052.7 Å$^3$, $Z$ = 4, $D_c$ = 2.85 g cm$^{-3}$, $T$ = −59 °C, $\mu$(Mo Kα) = 206.2 cm$^{-1}$, $\lambda$ = 0.710 69 Å, CAD4 diffractometer, 11 752 reflections measured, 9018 unique, and 6196 observed [$F_o \geq 4\sigma(F_o)$]. Structure solution was performed by direct methods, and all missing non-hydrogen atoms were located by successive difference Fourier syntheses; refinement of 386 parameters converged at $R$ = 0.0620 ($R_w$ = 0.0535), ($R = [\Sigma F_o - F_c]/\Sigma F_o$, $R_w = [\Sigma(F_o - F_c)^2/[wF_o2]^{1/2}$ with $w = [\sigma^2(F_o) + 0.000298F_o2]^{-1}$), using a split model of rigid groups for one $BF_4^-$ ion (SOF = 0.48/0.58); hydrogen atoms were included in idealized, fixed positions ($U_{iso}$ = 0.08); empirical absorption correction was applied ($T_{min}$ = 99.93%); maximum and minimum residual electron densities in the difference Fourier map were 6.21 and −3.98 e Å$^{-3}$ (located at the gold atoms), respectively.

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**Supplementary Material Available:** Tables giving full crystallographic details of the structure determination and tables of final fractional atomic coordinates, non-H atom anisotropic temperature factors, H atom isotropic temperature factors, bond lengths, and bond angles (20 pages). Ordering information is given on any current masthead page.

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