Polynuclear Gold(I) Complexes of Dendritic Amines: Formation of Terminal Tris[(triphenylphosphine)aurio(I)]ammonium Groups $-N(AuPPh_3)_3^{1+}$

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Dedicated to Professor W. Preetz on the occasion of his 60th birthday

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Gold(I) Complexes, Dendritic Amines, Gold(I) Complexes, Primary Amines

The reactions of dendritic amines $RN(CH_2CH_2CH_2NH_2)_2$ (R = Me, *c*-Hex, $PhCH_2$) and $N(CH_2CH_2NH_2)_3$ with tris[(triphenylphosphine)aurio(I)]oxonium tetrafluoroborate $[O(AuPPh_3)_3]^+BF_4^-$ in THF yield species with terminal imido cluster groups $-N(AuPPh_3)_3^{1+}$. The compounds have been obtained as stable crystalline solids in high yields and characterized by NMR spectroscopy as well as mass spectrometry and elemental analysis. The triply charged nonanuclear complex $[N(CH_2CH_2N(AuPPh_3)_3)_3]^{3+}$ exhibits major changes in the ^1H spectroscopic data and in the chemical properties as compared with compounds with dications $[RN(CH_2CH_2CH_2N(AuPPh_3)_3)_2]^{2+}$ (R = Me, *c*-Hex, $PhCH_2$). Excessive auration to give hypercoordinated species has not been observed.

Introduction

Although gold in its oxidation state +I possesses a closed shell electronic configuration ($[Xe]4f^{14}5d^{10}$), solid-state structures of both mono- and polynuclear gold(I) compounds show short Au···Au contacts near 3.0 Å which bear witness to attractive forces between the linearly two-coordinate gold(I) centres ("auriophilicity") [1]. These bonding relationships, which occur perpendicular to the principal axis, are unexpected in classical bonding concepts and have been rationalized on the basis of metal orbital energies modified by relativistic effects. In polynuclear gold complexes of the general type $[E(Au^IL)_n]$ or $[R-E(Au^IL)_n]$, with an interstitial main group element atom E, intramolecular Au···Au bonding interactions have been recognized as being synergistic in nature and to lead to gold clustering in hypercoordinated species (*e.g.* $[N(AuL)_5]^{2+}$; $[R-N(AuL)_4]^{2+}$) [2, 3].

"Auriophilicity" often determines the configuration and conformation of gold(I) compounds affecting *i.a.* the structure of the ligand "backbone". Through these changes *intra*molecular Au···Au networks are built, or *inter*molecular aggregates such as dimers, chains and layers are formed in the condensed phase [4, 5]. In this context dendritic (Greek: branched) molecules or dendrimers [6–8] appear to be particularly promising ligand systems, which allow a large number of both intra- and intermolecular Au···Au contacts. The tree-like dendrimer molecules are prepared by repetitive reactions ("cascade-synthesis") starting from an initiator core (generation 0), from which two or more identical branches are emanating, each of them containing further branch sites at its end. In a series of reaction cycles new generations can be created and a fractal, ball-like structure can evolve until further growth is limited by surface congestion. In contrast to "classical" polymers, dendrimers thus obey a highly controlled molecular architecture, which may result in materials with a new spectrum of properties.

Very little is known about dendrimer surface chemistry, and especially about the surface coordination chemistry. Studies have been reported on metal salts formed in the hydrolysis of ester-terminated dendrimers and on copper complexes of NH_2-terminated dendrimers, which yield deep purple solutions, but no details are available [7].

We have now employed $RN(CH_2CH_2CH_2NH_2)_2$ (R = Me, *c*-Hex, $PhCH_2$) and $N(CH_2CH_2NH_2)_3$ as the first generation of dendritic polyimide ligands for gold(I). In the present paper we describe the auration of the terminal (chain-end) primary amino groups, using the oxonium compound $[O(AuPPh_3)_3]^+BF_4^-$, to give branched imido gold clusters with end groups of the type

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$-N(AuPPh_3)_3^{1+}$ [9–14]. Solid state structures of such monocationic species usually feature a tetrahedral geometry around a central nitrogen atom, with short intramolecular Au···Au contacts. Already in the first generation of dendritic polyamines additional intermolecular Au···Au bonding interactions may occur, which can greatly stabilize the polynuclear systems.

Experimental

All experiments were carried our in an atmosphere of purified nitrogen with the exclusion of light, employing standard Schlenk techniques. The solvents were dried, saturated with nitrogen, and destilled before use.

NMR spectra were recorded on a Jeol-GX 400 spectrometer (deuterated solvents as internal standards, converted to TMS, for ^1H and ^{13}C; external aqueous H_3PO_4 for ^{31}P). Mass spectra were obtained by field desorption (FD; solvent CH_2Cl_2) or fast atom bombardment (FAB; matrix 4-nitrobenzyl alcohol) ionization. The elemental analyses were performed in the micro-analytical laboratory of this Institute.

N,N-Bis(3-aminopropyl)cyclohexylamine [15], N,N-bis(3-aminopropyl)benzylamine [16] and tris-[(triphenylphosphine)aurio(I)]oxonium tetrafluoroborate [17] were prepared according to published methods. N,N-Bis(3-aminopropyl)methylamine and N,N,N-tris(2-aminoethyl)amine were purchased from Aldrich and used without further purification.

$[MeN(CH_2CH_2CH_2N(AuPPh_3)_3)_2]^{2+}$ $[BF_4^-]_2$ (**3a**),
$[c\text{-}HexN(CH_2CH_2CH_2N(AuPPh_3)_3)_2]^{2+}$ $[BF_4^-]_2$ (**3b**),
$[PhCH_2N(CH_2CH_2CH_2N(AuPPh_3)_3)_2]^{2+}$ $[BF_4^-]_2$ (**3c**)

Typically, a suspension of $[O(AuPPh_3)_3]^+BF_4^-$ **2** (0.50 g, 0.34 mmol) in tetrahydrofuran (20 ml) was added to a solution of the diamine (**1a:** 24.6 mg, **1b:** 35.2 mg, **1c:** 37.5 mg; 0.17 mmol) in the same solvent (20 ml), and the reaction mixture was stirred for 3 h at room temperature. The resulting solution was then filtered over cellulose to remove impurities of colloidal gold. After reducing the filtrate in volume, precipitation by addition of ether gave waxy oils, which were dried *in vacuo* to leave colourless microcrystalline products. Yield: 0.37 g, 71% (**3a**); 0.39 g, 75% (**3b**); 0.35 g, 67% (**3c**).

Analysis for **3a** *($[C_{115}H_{105}Au_6N_3P_6][B_2F_8]$, 3070.4)*
Calcd C 44.98 H 3.45 N 1.37 P 6.05%,
Found C 44.72 H 3.56 N 1.48 P 5.70%.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2; RT): 29.2, s. ^1H NMR (CD_2Cl_2; RT): 1.22 [s, 3H, $C\underline{H}_3$]; 2.12 [quin, $^3J(HH)$ = 7.1, 4H, 2-$C\underline{H}_2$]; 2.55 [t, $^3J(HH)$ = 7.1, 4H, 1-$C\underline{H}_2$]; 4.18 [m, 4H, 3-$C\underline{H}_2$]; 7.24–7.27 [m, 36H, *m*-$C_6\underline{H}_5$]; 7.42–7.47 [m, 54H, *o/p*-$C_6\underline{H}_5$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2; RT): 42.4 [s, $\underline{C}H_3$]; 42.5 [s, C2]; 55.9 [s, C1]; 59.3 [s, C3]; 129.5 [d, $^1J(CP)$ = 58.6, C_{ipso}]; 129.7 [d, $^3J(CP)$ = 11.4, C_{meta}]; 132.3 [s, C_{para}]; 134.4 [d, $^2J(CP)$ = 13.7, C_{ortho}]. FD-MS [*m/z*]: 721.0 (2.3%, $[Au(PPh_3)_2]^+$); 1154.5 (4.7%, $[N(AuPPh_3)_5]^{2+}$); 1218.6 (9.5%, $[M-(AuPPh_3)]^{2+}$); 1377.0 (6.5%, $[(AuPPh_3)_6]^{2+}$); 1448.0 (100%, M^{2+}); 1520.1 (6.3%, $[M\text{-}3(AuPPh_3)]^+$); 1849.9 (8.3%, $[N(AuPPh_3)_4]^+$).

N,N-Bis(3-aminopropyl)methylamine: ^1H NMR ($CDCl_3$; RT): 1.22 [s, 3H, $C\underline{H}_3$]; 1.61 [quin, $^3J(HH)$ = 6.8, 4H, 2-$C\underline{H}_2$]; 2.21 [s, 4H, NH_2]; 2.39 [t, $^3J(HH)$ = 6.8, 4H, 1-$C\underline{H}_2$]; 2.73 [t, 4H, 3-$C\underline{H}_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$; RT): 42.0 [s, $\underline{C}H_3$]; 30.9 [s, C2]; 55.4 [s, C1]; 40.5 [s, C3].

Analysis for **3b** *($[C_{120}H_{113}Au_6N_3P_6][B_2F_8]$, 3138.5)*
Calcd C 45.92 H 3.63 N 1.34 P 5.92%,
Found C 46.47 H 3.86 N 1.49 P 5.86%.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2; RT): 29.3, s. ^1H NMR (CD_2Cl_2; RT): 0.70–1.90 [m, 10H, 2′,3′,4′,5′,6′-$C\underline{H}_2$-^{c}Hex]; 2.07 [quin, $^3J(HH)$ = 7.1, 4H, 2-$C\underline{H}_2$]; 2.33 [m, 1H, 1′-$C\underline{H}$-^{c}Hex]; 2.95 [m, 4H, 1-$C\underline{H}_2$]; 4.35 [m, 4H, 3-$C\underline{H}_2$]; 7.25–7.29 [m, 36H, *m*-$C_6\underline{H}_5$]; 7.43–7.49 [m, 54H, *o/p*-$C_6\underline{H}_5$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2; RT): 24.9 [s, C3′]; 26.1 [s, C4′]; 33.7 [s, C2′]; 42.2 [s, C2]; 44.6 [s, C1]; 56.8 [s, C1′]; 58.4 [s, C3]; 129.1 [d, $^3J(CP)$ = 11.5, C_{meta}]; 129.3 [d, $^1J(CP)$ = 58.4, C_{ipso}]; 131.8 [s, C_{para}]; 133.8 [d, $^2J(CP)$ = 13.7, C_{ortho}]. FD-MS [*m/z*]: 459.3 (100%, $[AuPPh_3]^+$); 721.0 (5.7%, $[Au(PPh_3)_2]^+$); 1154.5 (14.6%, $[N(AuPPh_3)_5]^{2+}$); 1377.7 (20.6%, $[(AuPPh_3)_6]^{2+}$); 1482.1 (3.4%, M^{2+}); 2045.3 (31.9%, $[M\text{-}2(AuPPh_3)]^+$).

N,N-Bis(3-aminopropyl)cyclohexylamine: ^1H NMR ($CDCl_3$; RT): 0.70–1.90 [m, 18H, 2′,3′,4′,5′,6′-$C\underline{H}_2$-^{c}Hex, 2-$C\underline{H}_2$, NH_2]; 2.33 [m, 1H, 1′-C2-^{c}Hex]; 2.73 [m, 8H, 1-$C\underline{H}_2$, 3-$C\underline{H}_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$; RT): 24.6 [s, C3′]; 25.7 [s, C4′]; 33.1 [s, C2′]; 33.8 [s, C2]; 44.4 [s, C1]; 40.1 [s, C3]; 56.4 [s, C1′].

Upon attempting to crystallize **3b** only a degradation product (**3b′**) was obtained from wet THF/ether after 3 weeks at room temperature. This material has only been characterized by an X-ray crystal structure determination.

All X-ray investigations were performed on an automated four-circle diffractometer CAD4 (ENRAF-NONIUS, Delft) with graphite-mono-

chromated MoK$_\alpha$ radiation at −80 °C. A colourless single crystal of $C_{67}H_{71}Au_3B_1F_4N_2O_1P_3$ (**3b**′×THF) with approximate dimensions 0.1×0.2×0.3 mm was sealed in a glass capillary. The lattice parameters were determined by refinement of the diffraction geometry of 25 precisely centered high-angle reflections and led to a triclinic cell with a = 12.878(1), b = 15.049(1), c = 18.434(1) Å, α = 100.23(1), β = 100.09(1), γ = 93.11(1)°, V = 3447.9 Å^3, Z = 2, d_{calc} = 1.629 g/cm^3. 12907 intensity data (unique) were collected with ω/θ scan in the θ range 2 to 27°. During the exposure time no loss of intensity was observed. The centrosymmetric space group P$\bar{1}$ was assumed for the structure solution with direct methods. After refinement with unique data and isotropic displacement factors the procedure for the empirical absorption correction (μ = 6.487 mm^{-1}) with the program DIFABS [19] was applied. The final full-matrix least-squares refinement (on F^2) with anisotropic displacement parameters for the Au, P, N and C(1) to C(9) atoms, phenyl rings and BF_4^- as rigid groups, positions of the H atoms in calculated idealized positions, led to R values of R_1 = 0.0729 and wR_2 = 0.1702 with $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_c|$ and $wR_2 = [\Sigma(w(F_o^2-F_c^2)^2/\Sigma(\omega(F_o^2)^2)]^{1/2}$, 6718 reflections with $F_o > 4\sigma(F_o)$, GooF (F^2) = 1.195, 21 restraints, 302 parameters, F(000) = 1636; largest difference peak and hole 1.828 and −1.351 e/Å^3 (near Au). Due to the poor crystal quality and disorder problems (especially C2, C3, N2; BF_4^-) the displacement parameters have unusual large values. Refinement in the non-centrosymmetric space group P1 revealed the same problems. Calculations were performed with the programs CADSHEL, SHELXS-86, SHELXL-93, and the SHELXTL-PLUS package [20]. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 58123, the names of the authors, and the journal citation.

Analysis for **3c** *($[C_{121}H_{109}Au_6N_3P_6][B_2F_8]$, 3146.5)*
Calcd C 46.19 H 3.49 N 1.34 P 5.91%,
Found C 45.68 H 3.87 N 1.48 P 5.62%.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2; RT): 29.2, s. ^1H NMR (CD_2Cl_2; RT): 2.11 [quin, ^3J(HH) = 7.1, 4H, 2-C$\underline{H}_2$]; 2.63 [t, ^3J(HH) = 7.1, 4H, 1-C$\underline{H}_2$]; 3.53 [s, 2H, 1′-C$\underline{H}_2$-benzyl]; 4.19 [m, 4H, 3-C$\underline{H}_2$]; 7.04–7.06 [m, 5H, $C_6\underline{H}_5$′-benzyl]; 7.22–7.26 [m, 36H, *m*-$C_6\underline{H}_5$]; 7.41–7.46 [m, 54H, *o*/*p*-$C_6\underline{H}_5$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2; RT): 42.2 [s, C2]; 51.9 [s, C1]; 58.6 [s, C3]; 59.2 [s, C1′]; 127.0 [s, C5′]; 128.6 [s, C3′]; 128.9 [s, C4′]; 129.6 [d, ^3J(CP) = 11.6, C_{meta}]; 129.7 [d, ^1J(CP) = 58.7, C_{ipso}]; 132.1 [s, C_{para}]; 134.2 [d, ^2J(CP) = 13.5, C_{ortho}]; 140.3 [s, C2′]. FAB-MS [*m*/*z*]: 459.0 (100%, $[AuPPh_3]^+$); 720.9 (76.8, $[Au(PPh_3)_2]^+$); 1376.9 (4.9%, $[(AuPPh_3)_6]^{2+}$); 1485.9 (6.0%, M^{2+}); 1729.8 (7.4%, $[M-Au(PPh_3)_2(AuPPh_3)]^+$); 2250.2 (4.3%, $[M-Au(PPh_3)_2]^+$).

N,N-Bis(3-aminopropyl)benzylamine: ^1H NMR ($CDCl_3$; RT): 1.01 [s, 4H, NH_2]; 1.60 [quin, ^3J(HH) = 6.8, 4H, 2-C$\underline{H}_2$]; 2.45 [t, ^3J(HH) = 6.8, 4H, 1-C$\underline{H}_2$]; 2.70 [t, 4H, ^3J(HH) = 6.8, 3-C$\underline{H}_2$]; 3.52 [m, 4H, 1′-C$\underline{H}_2$-benzyl]; 7.29 [m, 5H, $C_6\underline{H}_5$′-benzyl]. $^{13}C\{^1H\}$ NMR ($CDCl_3$; RT): 30.8 [s, C2]; 40.3 [s, C3]; 51.2 [s, C1]; 58.6 [s, C1′]; 126.6 [s, C5′]; 127.6 [s, C3′]; 128.6 [s, C4′]; 139.8 [s, C2′].

$[N(CH_2CH_2N(AuPPh_3)_3)_3]^{3+}[BF_4^-]_3$ (**5**)

Compound **5** was prepared using the procedure described for **3a–c:** Room temperature, extended reaction time (12 h), triamine **4** (22.6 mg, 0.16 mmol) and 3 equiv. of $[O(AuPPh_3)_3]^+BF_4^-$ (0.69 g, 0.47 mmol), yield 0.51 g, 73%.

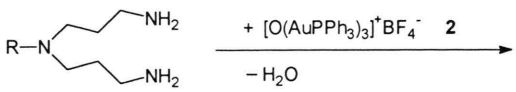
Analysis for **5** *($[C_{168}H_{147}Au_9N_4P_9][B_3F_{12}]$, 4533.95)*
Calcd C 44.50 H 3.27 N 1.24 P 6.15 Au 39.10%,
Found C 44.98 H 3.55 N 1.32 P 5.83 Au 39.60%.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2; RT): 29.0, s. ^1H NMR (CD_2Cl_2; RT): 3.10 [t, 6H, 1-C$\underline{H}_2$]; 4.43 [m, ^3J(HH) = 6.5, 6H, 2-C$\underline{H}_2$]; 7.09–7.13 [m, 54H, *m*-$C_6\underline{H}_5$]; 7.21–7.24 [m, 27H, *p*-$C_6\underline{H}_5$]; 7.31–7.37 [m, 54H, *o*-$C_6\underline{H}_5$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2; RT): 66.0 [s, C1]; 58.5 [s, C2]; 129.1 [d, ^1J(CP) = 58.9, C_{ipso}]; 129.3 [d, ^3J(CP) = 11.5, C_{meta}]; 131.9 [s, C_{para}]; 133.8 [d, ^2J(CP) = 13.5, C_{ortho}]. FAB-MS [*m*/*z*]: 459.7 (100%, $[AuPPh_3]^+$); 720.5 (78.5%, $[Au(PPh_3)_2]^+$); 1391.4 (3.1%, $[HN(AuPPh_3)_3]$); 1849.6 (3.7%, $[N(AuPPh_3)_4]^+$); 2179.2 (6.6%, $M^{3+} + BF_4^-$]).

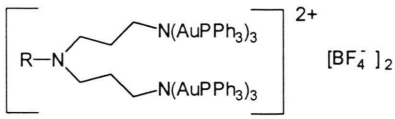
N,N,N-Tris(2-aminoethyl)amine: ^1H NMR ($CDCl_3$; RT): 1.31 [s, 6H, NH_2]; 2.49 [t, ^3J(HH) = 6.1, 6H, 1-C$\underline{H}_2$]; 2.73 [t, ^3J(HH) = 6.1, 6H, 2-C$\underline{H}_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$; RT): 40.0 [s, C2]; 57.8 [s, C1].

Results and Discussion

The branched polyamines chosen for this study, the N,N-bis(3-aminopropyl)amines **1a–c** and N,N,N-tris(2-aminoethyl)amine **4,** represent the



1a-c



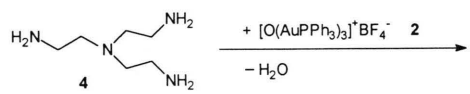
3a-c

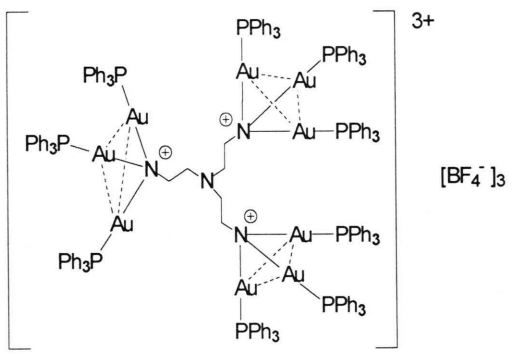
a: R = CH_3

b: R = c-Hex

c: R = $PhCH_2$

(1)





5

(2)

first generation of dendritic polypropylene- and polyethylene-imines, respectively.

The reaction of these polyfunctional species with the oxonium reagent $[O(AuPPh_3)_3]^+BF_4^-$ (**2**) in THF affords the complexes **3a–c** and **5** as colourless solids in high yield. In each case the terminal primary amino groups ($-NH_2$) have been found to form the corresponding organotris[(triphenylphosphine)aurio(I)]ammonium salts with terminal imido cluster groups of the type $-N(AuPPh_3)_3^{1+}$ (eq. (1), (2)).

The compounds are insensitive to air, moisture and light, and soluble in polar solvents. The solutions slowly decompose at ambient temperature with separation of colloidal gold. The triammonium salt **5** is the least stable of the compounds, probably due to the higher charge of the trication.

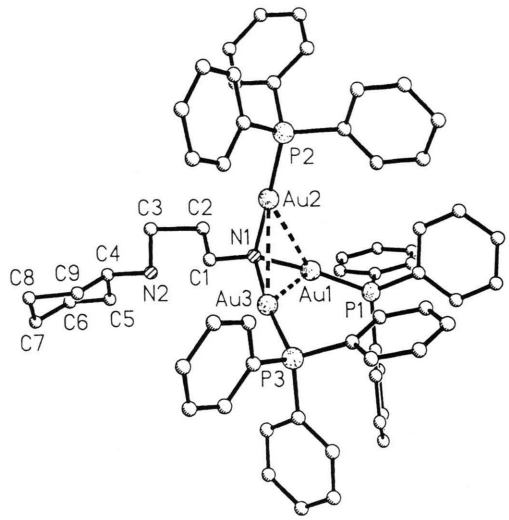


Fig. 1. Structure of the cation in compound **3b′**×THF.

The complexes have been characterized by means of NMR spectroscopy, mass spectrometry and elemental analysis. Attempts to grow single crystals suitable for an X-ray study have so far only lead to a degradation product of **3b** (**3b′**).

The molecular structure of the cation in **3b′** (with no crystallographic symmetry) is shown in Fig. 1. Beside the cation $[c\text{-Hex–NH–CH}_2\text{CH}_2\text{CH}_2\text{N(AuPPh}_3)_3]^+$, the triclinic cell contains the counter-anion BF_4^- and one equivalent of solvent (**3b′**×THF) in the asymmetric unit, with no unusual interionic or intermolecular contacts. As is evident from inspection of Table I, the structural parameter of the cation in **3b′** agree with those of the known imido gold clusters of the type $[R\text{–N(AuPPh}_3)_3]^+$. Short intramolecular Au··· Au bonding interactions near 3.0 Å between the linear two-coordinated gold(I) centres result in a distorted tetrahedral geometry around the

Table I. Selected bond lengths [Å] and angles [°] of compound **3b′** (for atomic numbering, see Fig. 1).

Au(1)···Au(2)	3.247(1)	Au(1)–N(1)–Au(2)	105.8(9)
Au(1)···Au(3)	2.952(1)	Au(1)–N(1)–Au(3)	93.2(7)
Au(2)···Au(3)	3.064(1)	Au(2)–N(1)–Au(3)	97.7(8)
Au(1)–N(1)	2.03(2)	C(1)–N(1)–Au(1)	122(2)
Au(2)–N(1)	2.04(2)	C(1)–N(1)–Au(2)	120(2)
Au(3)–N(1)	2.03(2)	C(1)–N(1)–Au(3)	113(2)
Au(1)–P(1)	2.241(6)	N(1)–Au(1)–P(1)	173.4(5)
Au(2)–P(2)	2.244(6)	N(1)–Au(2)–P(2)	178.2(5)
Au(3)–P(3)	2.224(6)	N(1)–Au(3)–P(3)	172.8(6)
N(1)–C(1)	1.51(4)		

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for compound **3b′**×THF.

Atom	*x*	*y*	*z*	U(eq)
Au(1)	1593(1)	2879(1)	3487(1)	65(1)
Au(2)	– 867(1)	2187(1)	2772(1)	64(1)
Au(3)	635(1)	3128(1)	1968(1)	65(1)
P(1)	3162(5)	2394(4)	3902(3)	65(2)
P(2)	–2093(4)	1001(4)	2526(3)	62(2)
P(3)	1159(5)	2782(4)	872(3)	67(2)
N(1)	211(13)	3288(13)	2991(10)	70(5)
N(2)	– 55(33)	5936(28)	4185(31)	249(27)
C(1)	– 131(34)	4220(27)	3249(20)	139(17)
C(2)	– 458(39)	4248(27)	3846(31)	189(22)
C(3)	– 999(41)	5260(31)	4105(38)	251(34)
C(4)	– 368(38)	6918(36)	4540(31)	171(18)
C(5)	438(31)	7525(23)	4937(23)	139(14)
C(6)	64(30)	8415(25)	5157(20)	133(13)
C(7)	– 431(36)	8808(27)	4463(30)	169(17)
C(8)	–1324(44)	8170(38)	3958(24)	206(23)
C(9)	– 874(43)	7172(35)	3792(27)	212(26)
C(11)	4196(11)	2934(11)	3541(9)	66(6)
C(12)	4111(12)	2847(12)	2769(8)	100(9)
C(13)	4908(15)	3241(14)	2478(7)	109(10)
C(14)	5790(13)	3723(13)	2960(10)	112(10)
C(15)	5875(11)	3811(12)	3732(10)	102(9)
C(16)	5078(13)	3417(12)	4022(7)	79(7)
C(21)	3589(13)	2602(12)	4910(7)	71(6)
C(22)	4161(14)	1998(10)	5272(10)	93(8)
C(23)	4217(15)	2983(14)	6462(7)	103(9)
C(25)	3645(15)	3588(11)	6100(9)	106(9)
C(26)	3331(13)	3397(11)	5324(10)	90(8)
C(31)	3168(12)	1180(8)	3596(8)	59(5)
C(32)	2309(10)	619(11)	3661(8)	76(7)
C(33)	2290(11)	– 315(10)	3436(9)	91(8)
C(34)	3130(14)	– 687(8)	3146(9)	88(8)
C(35)	3988(11)	– 126(11)	3080(9)	94(8)
C(36)	4007(10)	808(11)	3305(9)	88(8)
C(41)	–2656(13)	933(12)	3348(8)	70(6)
C(42)	–2918(14)	1733(10)	3752(10)	90(8)
C(43)	–3274(14)	1729(11)	4421(9)	104(9)
C(44)	–3367(14)	926(14)	4687(8)	95(8)
C(45)	–3105(15)	125(11)	4283(10)	109(10)
C(46)	–2750(14)	129(10)	3613(10)	98(9)
C(51)	–3193(12)	1099(12)	1801(8)	75(6)
C(52)	–4181(15)	645(12)	1746(10)	102(9)
C(53)	–4995(11)	697(14)	1155(12)	136(12)
C(54)	–4822(13)	1204(15)	619(10)	115(10)
C(55)	–3834(15)	1659(13)	675(9)	113(10)
C(56)	–3020(11)	1606(12)	1266(10)	82(7)
C(61)	–1610(12)	– 80(9)	2242(8)	63(6)
C(62)	–2314(9)	– 851(12)	1986(9)	83(7)
C(63)	–1936(14)	–1689(10)	1785(10)	101(9)
C(64)	– 854(15)	–1757(10)	1839(10)	113(10)
C(65)	– 150(10)	– 987(13)	2095(10)	106(9)
C(66)	– 528(11)	– 148(10)	2296(9)	85(7)
C(71)	1426(13)	1610(10)	703(10)	70(6)
C(72)	1391(14)	1125(13)	– 18(8)	109(10)
C(73)	1704(16)	249(13)	– 122(8)	135(12)
C(74)	2052(15)	– 142(10)	495(12)	114(10)
C(75)	2088(13)	343(12)	1217(9)	96(8)
C(76)	1775(13)	1219(11)	1320(7)	77(7)
C(81)	2339(11)	3431(11)	816(9)	70(6)
C(82)	2522(13)	4320(12)	1209(9)	81(7)
C(83)	3403(15)	4860(9)	1152(10)	116(10)
C(84)	4102(12)	4512(13)	701(11)	109(10)
C(85)	3919(13)	3623(14)	308(10)	114(10)
C(86)	3038(14)	3082(10)	365(9)	91(8)
C(91)	169(13)	2930(13)	77(9)	75(6)
C(92)	308(12)	3625(12)	– 313(11)	101(9)
C(93)	– 499(17)	3770(13)	– 876(11)	123(11)
C(94)	–1446(14)	3221(15)	–1048(10)	107(9)
C(95)	–1585(13)	2527(14)	– 659(12)	146(14)
C(96)	– 778(16)	2381(12)	– 96(11)	119(11)
B	4590(22)	7856(20)	1674(16)	28(31)
F(1)	5323(10)	8310(17)	2156(14)	113(13)
F(2)	3991(20)	7441(18)	1995(15)	142(16)
F(3)	4074(25)	8376(24)	1324(19)	219(25)
F(4)	4957(34)	7297(28)	1238(24)	533(78)
O(100)	2737(48)	6703(45)	3681(40)	362(30)
C(101)	2609(44)	5928(40)	2990(32)	214(22)
C(102)	3250(42)	5216(37)	3208(30)	201(21)
C(103)	3348(45)	5360(40)	4027(33)	219(23)
C(104)	2919(38)	6114(34)	4242(26)	171(17)

fourfold coordinated nitrogen atom. The Au–N–Au angles of 99.1° (average) differ considerably from the value of 109.5° expected for a regular tetrahedron. The atomic coordinates and equivalent isotropic thermal displacement parameters are listed in Table II.

Proton-, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra confirm the equivalence of the gilded amine functions in solutions of **3a–c** and **5,** respectively.

In the ^1H NMR spectra, the protons of the methylene groups immediately adjacent to terminal nitrogen (**3a–c:** 3-CH_2; **5:** 2-CH_2) give rise to multiplets without discernible fine structure, broadened by extensive ^{31}P couplings. The signals of the CH_2 protons further remote (**3a–c:** 2-CH_2, 1-CH_2; **5:** 1-CH^2) show the expected first order H–H multiplicity. There are two separate multiplets in the aromatic region of **3a–c** with an intensity ratio of 3:2, which are assigned to *ortho-/para-* and *meta*-H of the triphenylphosphine units, whereas all phenyl protons of **5** are resolved into three distinct sets (*ortho, meta, para*). Since this effect is known to be associated with increased charge density [12], these data also confirm the complete auration of all three primary amino groups to give **5.**

The ^1H and $^{13}C\{^1H\}$ chemical shift data of **3a–c** and **5** show a downfield shift of the respective

methylene resonances upon auration, as compared to the values obtained for the free ligands. With increasing distance in the alkyl-chains the deshielding effect of the triaurioammonium substituent ($-N(AuPPh_3)_3^{l+}$) is found to decrease. Thus the $^{13}C\{^1H\}$ singlets of the methylene groups attached to chain-end nitrogen (**3a–c:** 3-CH_2; **5:** 2-CH_2) are shifted to low field by about $\Delta\delta$ = +18 ppm, whereas the carbon resonances of the neighbouring CH_2 groups (**3a–c:** 2-CH_2; **5:** 1-CH_2) are only deshielded by about $\Delta\delta$ = +10 ppm, and the chemical shift values of the innermost carbon atoms of **3a–c** (1-CH_2) are similar to those in uncoordinated **1a–c.** The $^{13}C\{^1H\}$ subspectra of the triphenylphosphinegold(I) units of the products **3a–c** and **5** feature the known pattern of doublets for the phenyl carbon atoms. FD- and FAB mass spectra provide direct evidence for the existence of the dications in **3a–c.** The peaks at *m/z* = 1448.0 (100%, **3a**), *m/z* = 1482.1 (3.4%, **3b**) and *m/z* = 1485.9 (6.0%, **3c**) correspond to half the mass of the parent ions (M^{2+}), accompanied by *m/z* = 721 for $[Au(PPh_3)_2]^+$, *m/z* = 1103 for $[Ph_2P(AuPPh_3)_2]^+$, *m/z* = 1154 for $[N(AuPPh_3)_5]^{2+}$, *m/z* = 1377 for $[(AuPPh_3)_6]^{2+}$ and *m/z* = 1850 $[N(AuPPh_3)_4]^+$ as typical fragmentation/rearrangement products. The trication in **5** can be detected beside these typical fragmentation peaks by the FAB-MS signal at *m/z* = 2179.2 assigned to the species $[M^{3+} + BF_4^-]^{2+}$ (6.6%).

Conclusions

In the present study dendritic amines, *i.e.* the α,ω-diamines $RN(CH_2CH_2CH_2NH_2)_2$ (R = Me, *c*-Hex, $PhCH_2$) and the triamine $N(CH_2CH_2NH_2)_3$, have been employed vicariously for higher generations of polypropylene- and polyethylene-imines, to synthesize polynuclear species with terminal triaurioammonium groups $-N(AuPPh_3)_3^{l+}$.

The formation of highly aurated compounds, especially the nonanuclear trication $[N(CH_2CH_2N(AuPPh_3)_3)_3]^{3+}$ in **5,** which is the first known example of a tris(μ^3-triaurioimido) cluster, corroborates the crucial influence of synergistic Au···Au bonding interactions. Owing to their extensive heavy metal aggregates, these complexes are expected to be valuable in biochemical and medical diagnostics. Gold clusters have been employed successfully for these applications [18].

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