Dendrimer-Based Multinuclear Gold(I) Complexes

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In model reactions for the synthesis of phosphine-terminated tentacles of polyamine dendrimers, the amides $MeNHCOC_2H_4PPh_2$ (**2a**) and $(CH_2NHCOC_2H_4PPh_2)_2$ (**2b**) were prepared from the spacer phosphine (diphenylphosphino)propionic acid (**1**) and methylamine or ethylenediamine, respectively, using EDC [*N*-ethyl-*N*′-(3-(dimethylamino)propyl)carbodiimide hydrochloride] as a coupling agent. By the same procedure, the dendritic, multifunctional species DAB−PPI−$(NHCOC_2H_4PPh_2)_{16}$ (**5a**) and DAB−PPI−$(NHCOC_2H_4PPh_2)_{32}$ (**5b**) were obtained from diaminobutane−poly(trimethyleneamine) dendrimers. The purification of products **5a,b** was followed by GPC methods, and the compounds were identified by analytical and NMR spectroscopic data. Treatment of the diphenylphosphino-terminated compounds **2a,b** and **5a,b** with equivalent amounts of (dimethyl sulfide)gold(I) chloride afforded the corresponding mono-, di-, hexadeca-, and dotriacontanuclear gold(I) complexes **3a,b** and **6a,b**, respectively, with terminal (diphenylphosphine)gold(I) chloride groups (−PPh_2AuCl) in good yields as stable colorless solids. Full coverage of all ω-phosphine functions was accomplished as confirmed again by NMR spectroscopy. For further delineation of the configuration of the peptide−phosphine spacer tentacles, X-ray structure analyses were performed for $MeNHCOC_2H_4PPh_2AuCl$ (**3a**, triclinic, space group $P\bar{1}$) and $(CH_2NHCOC_2H_4PPh_2AuCl)_2$ (**3b**, monoclinic, space group $C2/c$). The conformation of the molecules and their packing can be rationalized on the basis of intermolecular NH···O hydrogen bonds, which in these cases exclude intra- and intermolecular $Au^I\cdots Au^I$ contacts.

Introduction

Dendrimer-based metal complexes are expected to be a particularly promising structural concept for new materials.[1] Compared with conventional metal-containing organic polymers,[2] dendritic (Greek: branched) cascade molecules offer a highly controlled architecture, which can be the basis for dendrimer-supported metal complexes with new properties. With the metal complexation limited to the terminal groups, all the coordination centers should be readily accessible for stoichiometric or catalytic reactions. Except for sporadic studies reported on polysiloxane-based nickel(II), polyamide-based gadolinium(III), polyphosphine-based palladium(I), and polyimine-based gold(I) dendrimer complexes,[3−6] the latter with chain-end imido gold clusters of the type $-N(Au^IPPh_3)_3]^+$, very little is known about surface coordination properties of dendrimers.

We recently introduced a new concept for surface-complexing phosphorus-functional dendrimers,[7] quite different from known systems containing phosphorus functions in the framework of the dendritic skeleton.[5,8] α-(Diphenylphosphino)acetic and *p*-(diphenylphosphino)benzoic acid have been employed as tailored "spacers" to functionalize preformed dendritic polyamines with terminal diphenylphosphino groups, which are ideal for complexation of transition metals in low oxidation states.

As an extension of this study, we have now employed β-(diphenylphosphino)propionic acid $HOOCC_2H_4PPh_2$ (**1**) in the synthesis of a new family of dendrimer-based multinuclear gold(I) complexes. The third and fourth generations of dendritic diaminobutane−poly(trimethyleneamine), DAB−PPI−$(NH_2)_{16}$ (**4a**) and DAB−PPI−$(NH_2)_{32}$ (**4b**), were coupled with β-(diphenylphosphino)propionic acid (**1**) to give systems with phosphino−amide tentacles of the type $-NHCOC_2H_4PPh_2$.

Suitable coupling conditions for the systhesis of *N*-alkylamides of **1** were probed and optimized using first methylamine and ethylenediamine as the amine components and *N*-ethyl-*N*′-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC) as an efficient carbodiimide coupling agent. The resulting diphenylphosphino-functionalized products **2a,b** were employed as ligands for gold(I) to give the corresponding phosphino−amide complexes $MeNHCOC_2H_4PPh_2AuCl$ (**3a**) and $(CH_2NHCOC_2H_4PPh_2AuCl)_2$ (**3b**), with $(Me_2S)AuCl$ as the source of the AuCl components.

This work was then extended to finally prepare DAB−PPI−$(NHCOC_2H_4PPh_2AuCl)_{16}$ (**6a**) and DAB−PPI−$(NHCOC_2H_4PPh_2AuCl)_{32}$ (**6b**), with 16 and 32 terminal (diphenylphosphido)gold(I) chloride groups, respectively.

It was hoped that structural work on the model compounds **3a,b** would give a clue as to the nature of inter- or intramolecular

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hydrogen bonds and/or Au···Au contacts, resembling the intertentacle interactions at the surface of the dendritic polyaurated products **6a,b**. Solid-state structures of gold(I) compounds often show short Au···Au contacts near 3.0 Å which bear witness to attractive forces associated with an energy on the order of hydrogen bonding effects (20 kJ/mol) and unexpected in the light of classical bonding concepts (Au^I: $[Xe]4f^{14}5d^{10}$).[9] More recent calculations including relativistic effects have demonstrated that these interactions can be rationalized as correlation phenomena.[10] The steric crowding in higher dendrimer generations should favor metal−metal contacts.

Experimental Section

All experiments were carried out in an atmosphere of purified nitrogen, employing standard Schlenk techniques. The solvents were dried, saturated with nitrogen, and distilled before use.

A JEOL GX 400 NMR spectrometer [solvent $CDCl_3$, except for **3b** (DMF/C_6D_6, 10/1); TMS as internal standard for ^1H and ^{13}C, external aqueous H_3PO_4 for ^{31}P] and a Finnigan MAT 90 mass spectrometer [FD source; solvent CH_2Cl_2] were employed. GPC analyses were carried out with a Waters GPC station (pump 510, UV detector 486, ultrastyragel 7.8 × 300 mm, polystyrene standards, M = 50−10 000 g/mol) in THF as a solvent. Melting points (sealed capillaries in a Büchi apparatus) are uncorrected. The elemental analyses were performed in the microanalytical laboratory of this Institute.

β-(Diphenylphosphino)propionic acid (**1**)[11] and (dimethyl sulfide)gold(I) chloride[12] were prepared according to published methods. Methylamine, ethylenediamine, and *N*-ethyl-*N*′-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC) were purchased from Aldrich. The diaminobutane−poly(trimethyleneamine) dendrimers DAB−PPI−$(NH_2)_{16}$ and DAB−PPI−$(NH_2)_{32}$ were purchased from DSM Fine Chemicals, P.O. Box 43, 6130 AA Sittard, The Netherlands.[13] β-(Diphenylphosphino)propionic acid (**1**) was purified by repeated recrystallization from aqueous 10% NaOH/2N HCl. Methylamine and ethylenediamine were distilled before use.

$MeNHCOC_2H_4PPh_2$ (2a) and [2a(AuCl)] (3a). A solution of methylamine (0.10 g, 3.27 mmol) in 20 mL of CH_2Cl_2 was added to a solution of 3.27 mmol of β-(diphenylphosphino)propionic acid (**1**, 0.85 g), EDC (0.63 g), and NEt_3 (0.33 mL) in the same solvent (30 mL). The reaction mixture was stirred for 3 h at ambient temperature, filtered to remove *N*-ethyl-*N*′-(3-(dimethylamino)propyl)urea, washed with saturated aqueous $NaHCO_3$ and NaCl, and then dried over $MgSO_4$. After removal of the solvent, purification by crystallization from ether/MeOH gave colorless needles (**2a**; yield 0.65 g, 73%).

$^{31}P\{^1H\}$-NMR ($CDCl_3$), δ: −15.2 [s]. ^1H-NMR ($CDCl_3$), δ: 2.24 [m, 2H, CH_2CP]; 2.37 [m, 2H, CH_2P]; 2.72 [d, $^3J_{HH}$ = 4.6, 3H, CH_3]; 5.80 [s, 1H, N*H*]; 7.28−7.45 [m, 10H, C_6H_5]. (All J values are in hertz.) $^{13}C\{^1H\}$-NMR ($CDCl_3$), δ: 23.4 [d, $^1J_{CP}$ = 12.0, *C*H_2P]; 26.2 [s, *C*H_3]; 32.5 [d, $^2J_{CP}$ = 18.4, *C*H_2CP]; 128.4 [d, $^3J_{CP}$ = 7.4, C_{meta}]; 128.7 [s, C_{para}]; 132.6 [d, $^2J_{CP}$ = 18.4, C_{ortho}]; 137.8 [d, $^1J_{CP}$ = 12.0, C_{ipso}]; 170.2 [d, $^3J_{CP}$ = 13.8, *C*O].

A solution of the product **2a** (0.44 g, 1.69 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of (dimethyl sulfide)gold(I) chloride (0.5 g, 1.69 mmol) in 20 mL of the same solvent, and the reaction mixture was stirred for 2 h at room temperature. Removal of the solvent and dimethyl sulfide in a vacuum left the crude product, which was dissolved in 5 mL of CH_2Cl_2, and the solution was filtered over cellulose to remove impurities of colloidal gold. Precipitation by addition of hexane gave a pure product, which was dried in vacuo to leave a colorless microcrystalline solid: yield 0.83 g, 95%; mp 213 °C. Anal. Calcd for **3a**, $C_{16}H_{18}AuClNOP$ (M_r = 503.7): C, 37.54; H, 3.77; N, 3.08. Found: C, 38.15; H, 3.60; N, 2.78.

$^{31}P\{^1H\}$-NMR ($CDCl_3$), δ: 29.9 [s]. ^1H-NMR ($CDCl_3$), δ: 2.45 [m, 2H, CH_2CP]; 2.66 [d, $^3J_{HH}$ = 4.8, 3H, CH_3]; 2.73 [m, 2H, CH_2P]; 6.03 [s, 1H, N*H*]; 7.35-7.63 [m, 10H, C_6H_5]. $^{13}C\{^1H\}$-NMR ($CDCl_3$), δ: 23.8 [d, $^1J_{CP}$ = 40.5, *C*H_2P]; 26.4 [s, *C*H_3]; 31.6 [d, $^2J_{CP}$ = 5.5, *C*H_2CP]; 128.5 [d, $^1J_{CP}$ = 60.7, C_{ipso}]; 129.2 [d, $^3J_{CP}$ = 12.0, C_{meta}]; 132.1 [d, $^4J_{CP}$ = 2.8, C_{para}]; 133.1 [d, $^2J_{CP}$ = 13.8, C_{ortho}]; 170.0 [d, $^3J_{CP}$ = 16.5, *C*O]. FD-MS (CH_2Cl_2), *m*/*z*: 503.2 (100%, $[M]^+$); 306.2 (5%, $[M - Au]^+$); 271.2 (36%, $[M - AuCl]^+$).

$(CH_2NHCOC_2H_4PPh_2)_2$ (2b) and [2b(AuCl)$_2$] (3b). Compounds **2b** and **3b** were prepared using the procedure described for **2a** and **3a**: Ethylenediamine (0.58 g, 9.68 mmol) was treated with 2 equiv (19.36 mmol) each of β-(diphenylphosphino)propionic acid (**1**, 5.00 g), EDC (3.71 g), and NEt_3 (2.8 mL). Subsequent purification by crystallization from diethyl ether/methanol gave colorless needles (**2b**; yield 4.00 g, 75%).

$^{31}P\{^1H\}$-NMR ($CDCl_3$), δ: −15.6 [s]. ^1H-NMR ($CDCl_3$), δ: 2.23 [m, 4H, CH_2CP]; 2.34 [m, 4H, CH_2P]; 3.27 [s, 4H, C_2H_4]; 6.42 [s, 2H, N*H*]; 7.28−7.39 [m, 20H, C_6H_5]. $^{13}C\{^1H\}$-NMR ($CDCl_3$), δ: 23.4 [d, $^1J_{CP}$ = 12.0, *C*H_2P]; 32.6 [d, $^2J_{CP}$ = 18.4, *C*H_2CP]; 39.9 [s, C_2H_4]; 128.51 [d, $^3J_{CP}$ = 6.4, C_{meta}]; 128.54 [s, C_{para}]; 132.6 [d, $^2J_{CP}$ = 18.4, C_{ortho}]; 137.7 [d, $^1J_{CP}$ = 12.9, C_{ipso}]; 172.3 [d, $^3J_{CP}$ = 13.5, *C*O].

Product **2b** (0.92 g, 1.70 mmol) was treated with Me_2SAuCl (1.00 g, 3.40 mmol) to give a colorless microcrystalline solid: yield 1.62 g, 95%; mp 154 °C. Anal. Calcd for **3b**, $C_{32}H_{34}Au_2Cl_2N_2O_2P_2$ (M_r = 1005.4): C, 38.22; H, 3.40; N, 2.79. Found: C, 37.82; H, 3.51; N, 2.73.

$^{31}P\{^1H\}$-NMR (DMF + C_6D_6), δ: 30.0 [s]. ^1H-NMR (DMF + C_6D_6), δ: 5.60 [s, 2H, N*H*]; 7.36−7.65 [m, 20H, C_6H_5]. $^{13}C\{^1H\}$-NMR (DMF + C_6D_6), δ: 23.8 [d, $^1J_{CP}$ = 40.0, *C*H_2P]; 31.7 [d, $^2J_{CP}$ = 5.5, *C*H_2CP]; 40.0 [s, C_2H_4]; 129.2 [d, $^1J_{CP}$ = 69.3, C_{ipso}]; 129.6 [d, $^3J_{CP}$ = 11.0, C_{meta}]; 132.3 [s, C_{para}]; 133.4 [d, $^2J_{CP}$ = 12.9, C_{ortho}]; 170.0 [d, $^3J_{CP}$ = 15.8, *C*O]. FD-MS (CH_2Cl_2), *m*/*z*: 969.6 (53%, $[M - Cl]^+$); 737.4 (100%, $[M - AuCl_2]^+$).

DAB−PPI−$(NHCOC_2H_4PPh_2)_{16}$ (5a) and [5a(AuCl)$_{16}$] (6a). Compounds **5a** and **6a** were prepared using the procedure described for **2a** and **3a**: DAB−PPI−$(NH_2)_{16}$ (**4a**, 1.94 mmol, 3.27 g) was treated with 20 equiv (38.7 mmol) each of β-(diphenylphosphino)propionic acid (10.00 g), EDC (7.42 g), and NEt_3 (5.6 mL). Subsequent purification by crystallization from ether/methanol (−30 °C) and benzene/hexane (slow diffusion by layering at room temperature) gave a yellowish oil (**5a**; yield 5.89 g, 55%).

GPC−UV (THF): t [min] = 22.40 (100%), M [g/mol] = 4479, M_z [g/mol] = 4406, M_w [g/mol] = 4145, M_z/M_w = 1.06. $^{31}P\{^1H\}$-NMR ($CDCl_3$), δ: −15.37 [s]. ^1H-NMR ($CDCl_3$), δ: 1−4 [m, 240H, 120 CH_2]; 7−8 [m, 160H, 32 C_6H_5]. H_{aliph}/H_{arom}: calcd, 1.50; found, 1.41. $^{13}C\{^1H\}$-NMR ($CDCl_3$), δ: 128.4 [d, $^3J_{CP}$ = 6.4, C_{meta}]; 128.6 [s, C_{para}]; 132.6 [d, $^2J_{CP}$ = 18.4, C_{ortho}]; 138.0 [d, $^2J_{CP}$ = 12.0, C_{ipso}]; 172.5 [d, $^3J_{CP}$ = 13.8, *C*O].

Product **5a** (1.17 g, 0.21 mmol) was treated with stoichiometric amounts of Me_2SAuCl (16 equiv, 1.00 g, 3.40 mmol) to give a colorless microcrystalline solid: yield 1.86 g, 95%; mp 95 °C. Anal. calcd for **6a**, $C_{328}H_{416}Au_{16}Cl_{16}N_{30}O_{16}P_{16}$ (M_r = 9249.5): C, 42.59; H, 4.53; N, 4.54; P, 5.36; Au, 34.07. Found: C, 39.45; H, 4.37; N, 4.19; P, 4.44; Au, 32.7.

$^{31}P\{^1H\}$-NMR ($CDCl_3$), δ: 29.85 [s]. ^1H-NMR ($CDCl_3$), δ: 1−4 [m, 240H, 120 CH_2]; 7−8 [m, 160H, 32 C_6H_5]. H_{aliph}/H_{arom}: calcd, 1.50; found, 1.47. $^{13}C\{^1H\}$-NMR ($CDCl_3$), δ: 128.6 [d, $^1J_{CP}$ = 60.7, C_{ipso}]; 129.2 [d, $^3J_{CP}$ = 12.0, C_{meta}]; 132.0 [s, C_{para}]; 133.1 [d, $^2J_{CP}$ = 13.8, C_{ortho}]; 170.2 [d, $^3J_{CP}$ = 15.6, *C*O].

DAB−PPI−$(NHCOC_2H_4PPh_2)_{32}$ (5b) and [5b(AuCl)$_{32}$] (6b). Compounds **5b** and **6b** were prepared using the procedure described for **2a** and **3a**: DAB−PPI−$(NH_2)_{16}$ (**4b**, 0.97 mmol, 3.40 g) was treated with 40 equiv (38.7 mmol) each of β-(diphenylphosphino)propionic acid (10.00 g), EDC (7.42 g), and NEt_3 (5.6 mL). Subsequent purification by crystallization from ether/methanol (−30 °C) and benzene/hexane (slow diffusion by layering at room temperature) gave a yellowish oil (**5b**; yield 5.75 g, 55%).

GPC−UV (THF): t [min] = 22.08 (91%), M [g/mol] = 5459, M_z [g/mol] = 5797, M_w [g/mol] = 5459, M_z/M_w = 1.06. $^{31}P\{^1H\}$-NMR ($CDCl_3$), δ: −15.40 [s]. ^1H-NMR ($CDCl_3$), δ: 1−4 [m, 496H, 248

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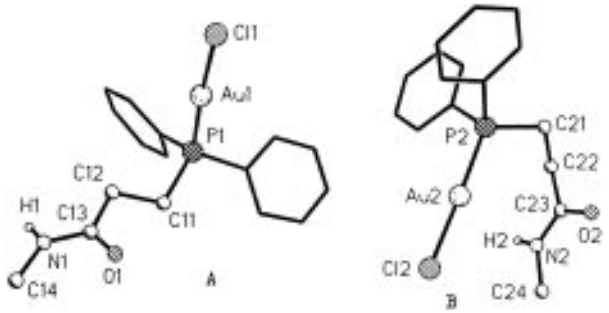


Figure 1. Molecular structures of the two crystallographically independent molecules **A** and **B** of compound **3a** with atomic numbering (CH_3, CH_2, and phenyl hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−P1 (Au2−P2) 2.230(2) (2.225(2)), Au1−Cl1 (Au2−Cl2) 2.278(2) (2.276(3)), P1−C11 (P2−C21) 1.810(9) (1.844(8)), C11−C12 (C21−C22) 1.529(12) (1.540(11)), C12−C13 (C22−C23) 1.508(11) (1.509(12)), C13−O1 (C23−O2) 1.219(11) (1.224(10)), C13−N1 (C23−N2) 1.331(11) (1.318(12)), N1−C14 (N2−C24) 1.454(11) (1.449(13)); Cl1−Au1−P1 (Cl2−Au2−P2) 176.09(8) (177.75(12)). For hydrogen bonds see Table 2.

CH_2]; 7−8 [m, 320H, 64 C_6H_5]. H_{aliph}/H_{arom}: calcd, 1.55; found, 1.43. $^{13}C\{^1H\}$-NMR ($CDCl_3$), δ: 128.4 [d, $^3J_{CP} = 6.4$, C_{meta}]; 128.5 [s, C_{para}]; 132.6 [d, $^2J_{CP} = 18.4$, C_{ortho}]; 138.1 [d, $^2J_{CP} = 12.0$, C_{ipso}]; 172.5 [d, $^3J_{CP} = 13.8$, *C*O].

Product **5b** (1.19 g, 0.11 mmol) was treated with stoichiometric amounts of Me_2SAuCl (32 equiv, 1.00 g, 3.40 mmol) to give a colorless microcrystalline solid: yield 1.88 g, 95%; mp 95 °C. Anal. Calcd for **6b**, $C_{664}H_{848}Au_{32}Cl_{32}N_{62}O_{32}P_{32}$ ($M_r = 18\,639.2$): C, 42.78; H, 4.59; N, 4.66; P, 5.32; Au, 33.82. Found: C, 38.55; H, 4.19; N, 4.38; P, 4.52; Au, 32.3.

$^{31}P\{^1H\}$-NMR ($CDCl_3$), δ: 29.75 [s]. ^{1}H-NMR ($CDCl_3$), δ: 1−4 [m, 496H, 248 CH_2]; 7−8 [m, 320H, 64 C_6H_5]. H_{aliph}/H_{arom}: calcd, 1.55; found, 1.46. $^{13}C\{^1H\}$-NMR ($CDCl_3$), δ: 128.6 [d, $^1J_{CP} = 60.5$, C_{ipso}]; 129.1 [d, $^3J_{CP} = 12.0$, C_{meta}]; 131.9 [s, C_{para}]; 132.9 [d, $^2J_{CP} = 13.8$, C_{ortho}]; 170.1 [d, $^3J_{CP} = 16.5$, *C*O].

Structural Data. Suitable crystals of **3a** and **3b** were mounted in glass capillaries 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 for both compounds. Diffraction intensities were corrected for Lp and absorption effects. The thermal motion of all non-hydrogen atoms was treated anisotropically. All phenyl, methyl, and methylene hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atom. The N−*H* atoms were located and included with fixed isotropic contributions ($U_{iso(fix)} = 0.08$ Å^2). Crystals of compounds **3a** and **3b** contain two crystallographically independent molecules, which show only marginal differences in dimensions but different conformations, as shown in Figures 1 and 2. Further information on crystal data, data collection, and structure solution and refinement is summarized in Table 1. Hydrogen bonds in the crystals of **3a** and **3b** are listed in Table 2. Important interatomic distances and angles are summarized in the corresponding figure captions.

Results and Discussion

The reactions of methylamine and ethylenediamine with *β*-(diphenylphosphino)propionic acid (**1**), in the presence of *N*-ethyl-*N*′-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC) and triethylamine as coupling agents, result in quantitative formation of the corresponding diphenylphosphino amides **2a,b** (Scheme 1).

The branched polyamines DAB−PPI−$(NH_2)_{16}$ (**4a**) and DAB−PPI−$(NH_2)_{32}$ (**4b**), with 16 and 32 terminal primary amino groups, respectively, afford the corresponding multifunctional species **5a,b**, when treated with the same reagents (Schemes 2 and 3).

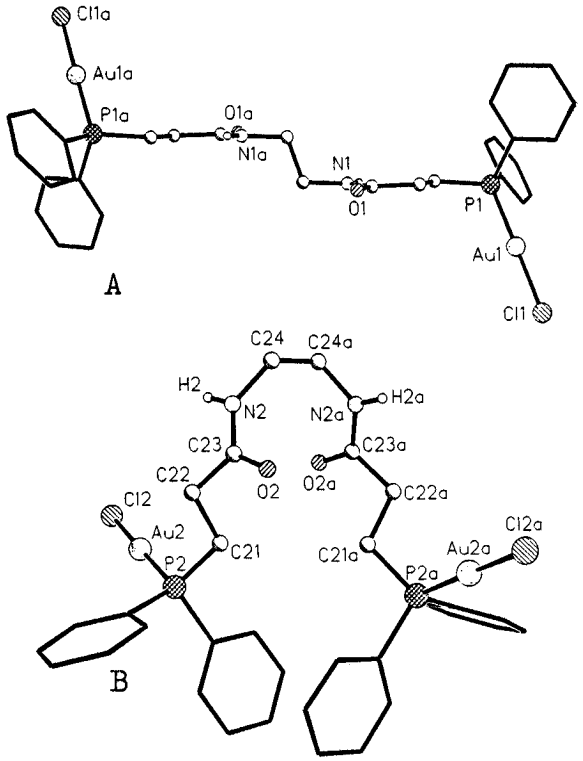


Figure 2. Molecular structures of the two crystallographically independent molecules **A** and **B** of compound **3b** with atomic numbering (CH_3, CH_2, and phenyl hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−P1 (Au2−P2) 2.229(2) (2.228(2)), Au1−Cl1 (Au2−Cl2) 2.280(2) (2.284(2)), P1−C11 (P2−C21) 1.822(6) (1.820(7)), C11−C12 (C21−C22) 1.501(9) (1.535(10)), C12−C13 (C22−C23) 1.518(9) (1.505(9)), C13−O1 (C23−O2) 1.238-(8) (1.235(8)), C13−N1 (C23−N2) 1.331(8) (1.339(9)), N1−C14 (N2−C24) 1.435(8) (1.448(8)), C14−C14a (C24−C24a) 1.533(14) (1.539(13)); Cl1−Au1−P1 (Cl2−Au2−P2) 178.90(7) (176.03(7)). For hydrogen bonds see Table 2.

After completion of the reactions in CH_2Cl_2, aqueous workup to remove the EDC byproduct (a urea derivate), and crystallization from ether/MeOH, the products are obtained in about 70% yield as colorless needles (**2a,b**) and yellowish oils (**5a,b**), soluble in most common organic solvents. In the case of the polychelate ligands **5a,b**, remaining traces of the coupling agents and incompletely functionalized defect species have to be removed by a further purification step (benzene/hexane).

Treatment of the phosphino amides **2a,b** and **5a,b** with Me_2SAuCl gives the mono-, di-, hexadeca-, and dotriacontanuclear gold(I) complexes **3a,b** and **6a,b**, respectively, in 95% yield, with liberation of dimethyl sulfide. In each case, all the terminal diphenylphosphino groups have been found to be engaged as coordination sites for the gold(I) chloride units. None of the amido or imino functions are employed in coordination to gold(I). The complexes are obtained as colorless solids (from CH_2Cl_2/hexane), stable to air and moisture but light-sensitive, especially in solution.

The analytical and spectroscopic data of **2a,b**, **3a,b**, **5a,b**, and **6a,b** are in good agreement with the proposed stoichiometries and structures (Experimental Section). Compounds **3a,b** have also been characterized by X-ray diffraction.

The GPC chromatograms of the purified polyfunctional ligands **5a,b** show only one major peak, indicating the successful removal of almost all the residues of the coupling agents. Discrepancies between calculated and found elemental analysis data are due to traces of impurities and inclusions of solvent. Since linear standards were used for GPC analyses, the GPC peaks of the spheric molecules **5a** ($M = 5531$ g/mol) and **5b**

Table 1. Crystal Data and Details of the Data Collection and Structure Solution and Refinement for Compounds **3a** and **3b**

	3a	**3b**
	Crystal Data	
formula	$C_{16}H_{18}NOPAuCl$	$C_{32}H_{34}N_2O_2P_2Au_2Cl_2$
M_r	503.72	1005.43
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ [No. 2]	$C2/c$ [No. 15]
a (Å)	9.114(1)	21.242(2)
b (Å)	12.733(2)	18.428(3)
c (Å)	18.501(3)	18.422(3)
α (deg)	99.98(1)	90
β (deg)	99.47(1)	96.82(1)
γ (deg)	109.72(1)	90
V (Å^3)	1932.1	7160.2
ρ_{calc} (g cm^{-3})	1.731	1.865
Z	4	8
F(000) (e)	960	3824
μ(Mo Kα) (cm^{-1})	78.09	84.29
	Data Collection	
diffractometer	Enraf-Nonius CAD4	
radiation	Mo Kα	Mo Kα
λ(Mo Kα) (Å)	0.710 69 (graphite monochromator)	
T (°C)	−59	−59
scan mode	$\theta-\theta$	$\theta-\theta$
hkl range	+11,±16,±23	+28,±24,±24
$((\sin\theta)/\lambda)_{max}$ (Å^{-1})	0.64	0.66
no. of measd reflns	8391	8571
no. of unique reflns	8332	8571
no. of obsd reflns	5968	6275
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$
abs cor	DIFABS	DIFABS
	Refinement	
no. of refined params	379	379
structure soln	Patterson methods	Patterson methods
H atoms (found/calcd)	2/34	2/32
R1[a]	0.0418	0.0382
wR2[b]	0.0983	0.0881
$(\text{shift/error})_{max}$	<0.001	<0.001
ρ_{fin}(max/min (e Å^{-3})	+2.06/−1.31[c]	+3.84/−0.89[c]

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$; $w = q/\sigma^2(F_o^2) + (ap)^2 + bp$; $p = \max(F_o^2,0) + 2F_c^2/3$; $a = 0.0502$ (**3a**), 0.0464 (**3b**); $b = 11.64$ (**3a**), 54.89 (**3b**). [c] Residual electron densities located at Au atoms.

Table 2. Hydrogen Bonds in the Structures of **3a** and **3b**[a]

compd	D−H···A	D−H, Å	H···A, Å	D···A, Å	D−H···A, deg
3a	N1−H1···O2^{i}	0.860	1.970	2.816	167.6
	N2−H2···O1^{ii}	0.860	1.933	2.791	174.8
3b	N1−H1···O2^{iii}	0.860	2.019	2.823	155.1
	N2−H2···O1^{i}	0.860	1.960	2.813	171.6

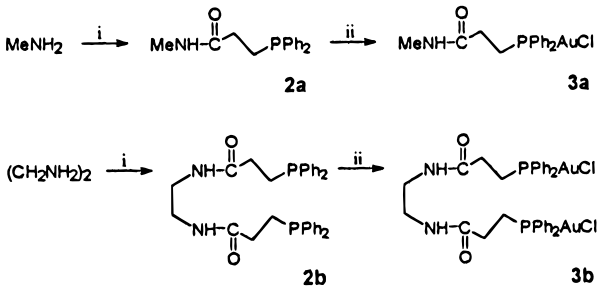
[a] Symmetry positions of atoms A: (i) $x-1, y+1, -z$; (ii) $x, y-1, z$; (iii) $x, y, z+1$; (iv) $x, -y, z-0.5$.

($M = 11202$ g/mol) appear at lower molar masses, $M_{\mathbf{5a}} = 4479$ g/mol and $M_{\mathbf{5b}} = 5459$ g/mol, due to the long retention times.

Proton-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR data confirm the virtually complete functionalization of all primary amines (to give **5a,b**) and auration (to give **6a,b**). In the $^{31}P\{^1H\}$-NMR spectra of **5a,b** and **6a,b**, the 16 and 32 equivalent diphenylphosphino groups, respectively, give rise to singlets, indicating the absence of any defect species, except for the traces of phosphine oxides detected at +34 ppm. Upon AuCl complexation these low-intensity signals remain unchanged, both in chemical shift and in relative intensity, whereas the main signals show a significant downfield shift from $\delta_{\mathbf{5a}} = -15.4$ ppm to $\delta_{\mathbf{6a}} = +29.9$ ppm ($\Delta\delta \approx +45$ ppm) and from $\delta_{\mathbf{5b}} = -15.4$ ppm to $\delta_{\mathbf{6b}} = +29.8$ ppm ($\Delta\delta \approx +45$ ppm), respectively.

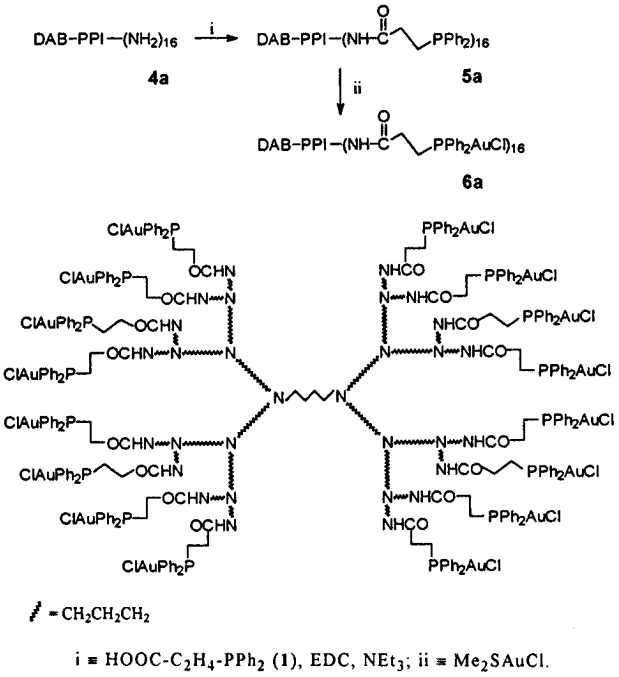
In the $^{13}C\{^1H\}$-NMR spectra of **5a,b** and **6a,b**, the ipso, ortho, meta, and para phenyl-C signals can be readily identified as distinct sets, but signal superpositions of similar CH_2 groups make assignment of most aliphatic resonances tentative.

Scheme 1



i = HOOC-C_2H_4-PPh_2 (**1**), EDC, NEt_3; ii = Me_2SAuCl.

Scheme 2



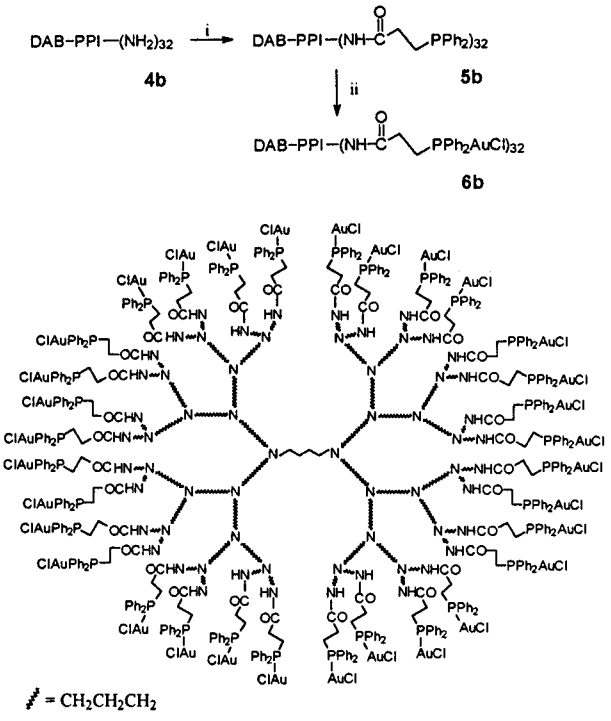
i = HOOC-C_2H_4-PPh_2 (**1**), EDC, NEt_3; ii = Me_2SAuCl.

Assuming similar T_1 values for aliphatic and aromatic protons, the observed ratio of intensities H_{aliph}/H_{arom} in the ^{1}H-NMR spectra of **5a,b** and **6a,b** corroborate the successful polyfunctionalization of the dendrimers. Note that all phenyl groups present in the products have been introduced by β-(diphenylphosphino)propionic acid (**1**) as a spacer and are thus a direct measure of the functionalization.

Solvent-free single crystals of $MeNHCOC_2H_4PPh_2AuCl$ (**3a,** triclinic, space group $P\bar{1}$) and $(CH_2NHCOC_2H_4PPh_2AuCl)_2$ (**3b,** monoclinic, space group $C2/c$) were obtained from benzene/diethyl ether and DMF/diethyl ether, respectively. An inspection of the data in the captions to Figures 1 and 2 shows that most of the structural parameters of **3a,b** agree generally quite well with those observed for comparable gold(I) complexes of phosphino amides.[7]

There are two independent molecules with different conformations (**A**, **B**) in the asymmetric unit of compound **3a**, and likewise in the asymmetric unit of compound **3b**. The molecular structures of both species **A** and **B** of **3a** (which have no crystallographic symmetry) are shown in Figure 1. Both molecules are mainly distinguished by their O1−C13−C12−C11 (+38.4°) and O2−C23−C22−C21 (−49.2°) dihedral angles. Intermolecular NH···O hydrogen bonds direct the

Scheme 3



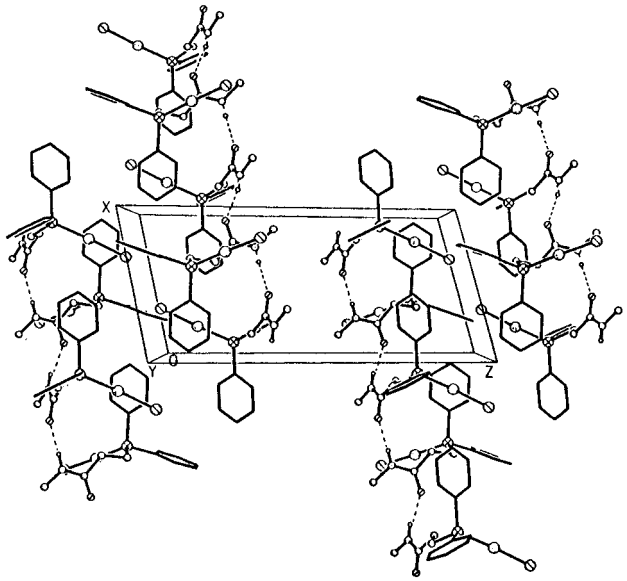


Figure 3. Crystal packing in the unit cell of **3a** showing the intermolecular hydrogen bonds (see also Table 2).

aggregation of the molecules in the solid state to give chainlike structures (Figure 3, Table 2).

Both species **A** and **B** of the formula **3b** as well as of **3a** adopt conformations which allow utilization of all NH and C═O groups for intermolecular hydrogen bonds (Figures 2 and 4, Table 2). The conformers of **3b** differ significantly in symmetry. While molecule **A** exhibits an inversion center (point group C_i), a rotation axis describes the symmetry of molecule **B** (point group C_2).

It appears that the hydrogen-bonding networks of **3a,b** are holding the PAuCl groups apart, thus overruling possible gold−gold contacts, which are common in solid-state structures of $-C_2H_4PPh_2Au^ICl$ compounds.[14] This result is perhaps not unexpected since the molecules **3a,b** with one PAuCl unit per NHCO amide group can support only *one* Au···Au contact but

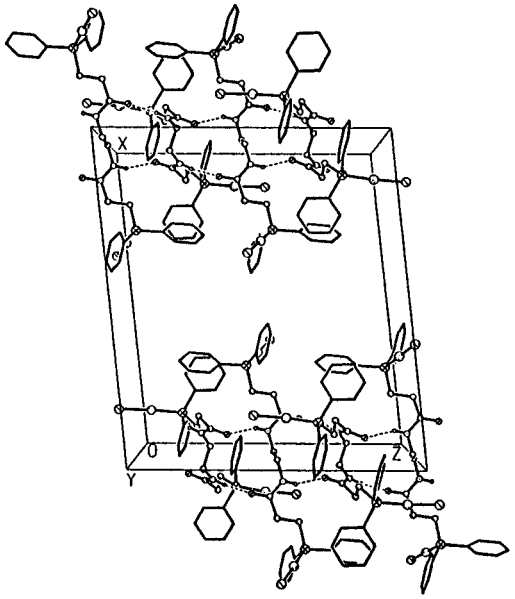


Figure 4. Crystal packing in the unit cell of **3b** showing the intermolecular hydrogen bonds (see also Table 2).

up to *two* NH···O hydrogen bonds. Thus aggregation via gold−gold interactions is not to be expected, although both types of secondary bonding are of comparable energy (20 kJ/mol).[9]

In multinuclear complexes **6a,b** a combination of intertentacle N−H···O and Au^I···Au^I bonding is more likely; especially for complex **6b**, with its compact surface of 32 terminal (diphenylphosphido)gold(I) groups, the peripheral network must include Au···Au contacts, complementary to the peptide hydrogen-bonding framework. Luminescence and EXAFS studies are under way to clarify this point.

Conclusions

In the present study we have established a new concept for the preparation of dendritic amines/amides with terminal phosphino donor functions for surface complexation. The third and fourth generations of dendritic diaminobutane−poly(trimethyleneamines), DAB−PPI−$(NH_2)_{16}$ and DAB−PPI−$(NH_2)_{32}$, and the model amines methylamine and ethylenediamine were employed for the functionalization with peripheral diphenylphosphino groups. Their chain-end primary amino groups can be coupled with β-(diphenylphosphino)propionic acid as a spacer suitable for auration to give the corresponding mono-, di-, hexadeca-, and dotriacontanuclear species with terminal (diphenylphosphido)gold(I) chloride groups ($-NHCOC_2H_4PPh_2$-AuCl). These multinuclear gold(I) complexes represent a new type of metal-containing polymer of a well-defined, probably spherical structure with branched dendrimer molecules as supporting matrices. Apart from potential applications of the new polychelate ligands **5a,b** in catalysis, the polynuclear gold(I) complexes **6a,b** are expected to be valuable in biochemical diagnostics and imaging and in medicine as antiinflamatory and antitumor drugs. Gold(I) compounds have been employed very

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succesfully for treatment of rheumatoid diseases.[15] According to established formulations, the chloride atoms in compounds **6a,b** should be substituted by thiolate ligands for optimized performance.

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Supporting Information Available: Listings of crystallographic data and data collection and refinement details, atomic positional parameters, anisotropic thermal parameters, bond distances, and bond angles (14 pages). Ordering information is given on any current masthead page.

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