Regioselective Gold Complexation within the Cascade Structure of Phosphorus-Containing Dendrimers

Christophe Larré, Bruno Donnadieu, Anne-Marie Caminade,* and Jean-Pierre Majoral*

Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday

Abstract: The construction of dendritic and polydendritic macromolecules which incorporate P=N−P=S, P=N−P=N−P=S, and $-PR_2$ ligands in selected generations within the cascade structure is reported. Complexation of these internal units with [AuCl(tht)] allows the regioselective grafting of up to 90 gold atoms in different layers. The X-ray structure of a first-generation dinuclear complex is described.

Keywords: dendrimers · gold · host–guest chemistry · phosphorus · S ligands

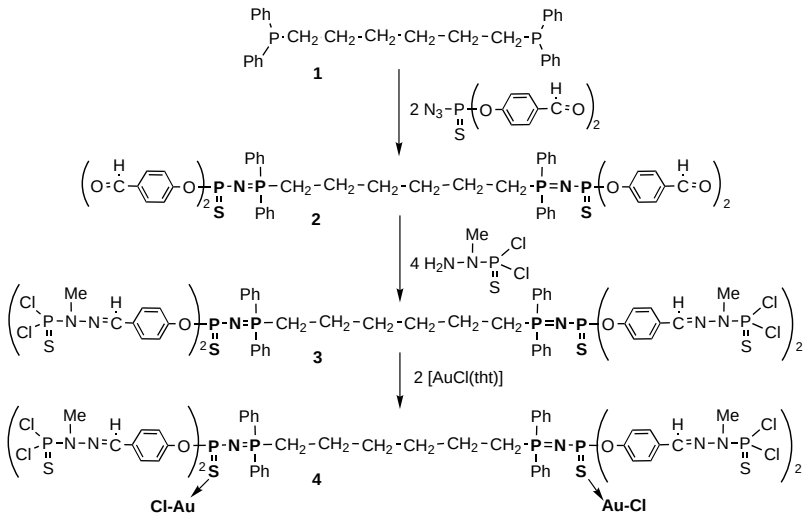
Introduction

Metalladendrimers constitute a very interesting class of macromolecules which can exhibit, in addition to the unique physical and chemical behavior of organic or inorganic dendrimers,[1a–f] useful properties in different areas, such as catalysis, electrochemistry, and photophysics, to name just a few. Metal centers can be grafted onto the surface or within dendrimers and have been shown to act as connectors or branching centers.[1e] Among all the metalladendrimers reported up to now, very little is known about dendrimer-based multinuclear gold(I) complexes. Coordination of the free phosphine core of a phosphorus-containing dendrimer of generation 2 with gold(I) was reported first.[2] Full coverage of the dendrimers with 16 and 32 ω-phosphine chain-ends of generation 2 and 3 was accomplished with $[Me_2SAuCl]$.[3] Recently, we prepared dendrimers containing thousands of terminal $-P(Ph)_2AuCl$ groups (generation 10); the gold complexes were imaged by high-resolution electron microscopy.[4] Therefore, gold can be introduced either at the core or on the surface of phosphorus-containing dendrimers.

We report herein on the first examples of regioselective gold complexation *into the internal layers* of dendritic and polydendritic macromolecules, with complexation taking place on nonconventional P=N−P=N−P=S fragments or P=N−P=S groups, or on more classical CH_2PPh_2 moieties. Up to 90 AuCl units can be grafted selectively within the cascade structure.

Results and Discussion

Two P=N−P=S linkages are first introduced into the cascade structure of a dendrimer of generation 1 (Scheme 1). Addition of 2 equivalents of [AuCl(tht)] to a dichloromethane solution of **3** gives the dinuclear complex **4** quantitatively. The



Scheme 1. Synthesis of the dinuclear gold complex dendrimer **4**.

reaction can be easily monitored by ^{31}P NMR: the two doublets due to the P=N−P=S fragments in **3** at $\delta = 20.9$ (CH_2PN) and 51.9 (N−P=S, $^2J(P,P) = 35$ Hz) disappear and are replaced by two new doublets in **4** at $\delta = 22.6$ (CH_2PN) and 34.9 (N−P=S, $^2J(P,P) = 27.4$ Hz) due to the two

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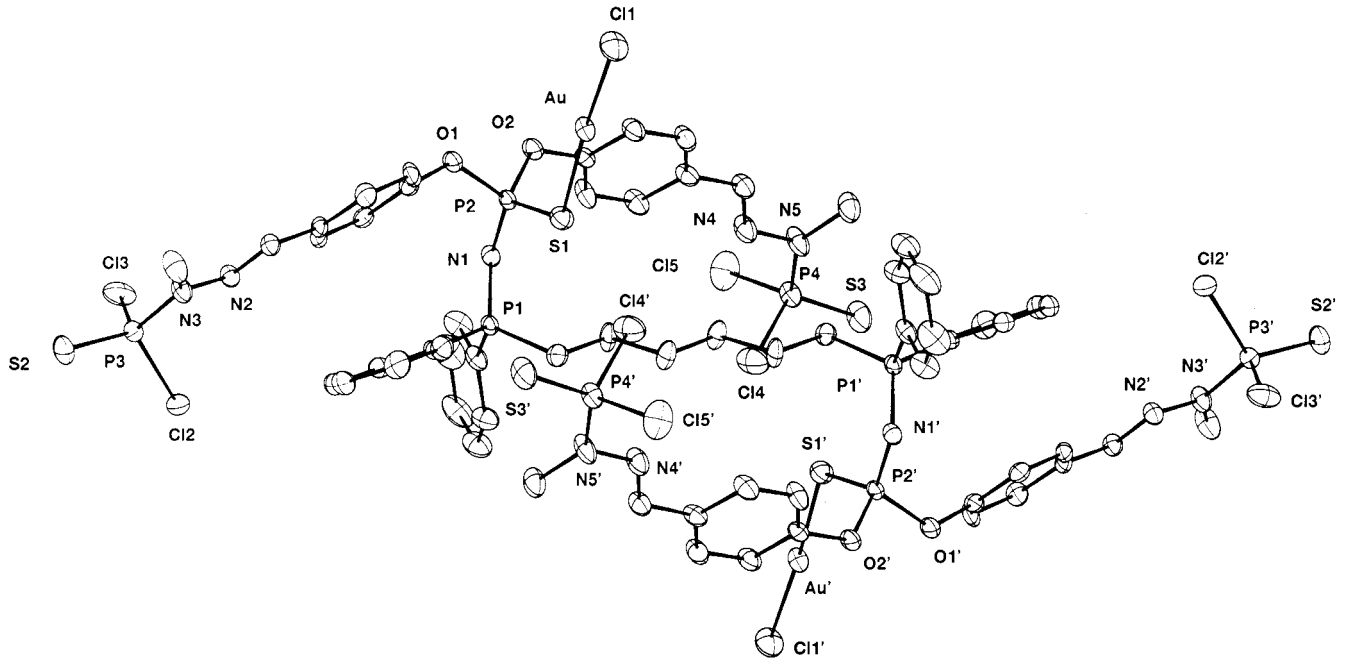


Figure 1. CAMERON drawing of **4**. Selected bond lengths [Å] and angles [°]: P2–S1 2.007(2), P3–S2 1.909(2), S1–Au 2.266(1), P2–N1 1.561(4), N1–P1 1.592(4), P1-N1-P2 138.5(3), P2-S1-Au 107.14(6).

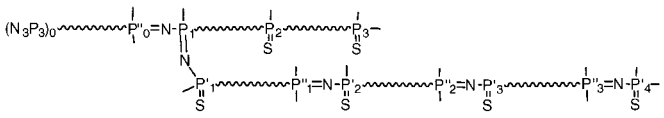
P=N–P=S →AuCl moieties. Interestingly, no complexation occurs on the ends of the $P(S)Cl_2$ chains, as shown by ^{31}P NMR: the same chemical shift ($\delta = 62.1$) is detected for these groups in **3** and **4**. An X-ray crystallographic study confirmed the structure of **4**. The CAMERON drawing of **4** is reproduced in Figure 1 and significant bond lengths and angles are given in the caption.

Hence, it appears that incorporation of P=N–P=S units into the framework of a dendrimer allows facile complexation of gold. Such a reaction is extended to the complexation of six AuCl groups within the cascade structure of **5**, a dendrimer of generation 3 (Table 1), in which six P=N–P=S units were located by construction on generation 1 (Scheme 2).[5]

Treatment of **5** (1 equivalent) in THF with six equivalents of [AuCl(tht)] in THF led to the hexanuclear gold complex **6** (Table 1). Such a complexation provokes the same marked shielding of the ^{31}P chemical shift of the N–P=S groups ($\Delta\delta =$ 17 ppm) and an analogous slight deshielding of the signal due to the CH_2P–N groups ($\Delta\delta = 1.5$ ppm) as that detected for the **3** →**4** transformation. No significant variation of chemical shifts was found for the phosphorus groups located at the core and on generations 2 and 3.

Abstract in French: *La construction de macromolécules dendritiques et polydendritiques ayant, pour certaines générations, à l'intérieur de la structure-cascade, des ligands P=N–P=S, P=N–P=N–P=S et PR_2 est décrite. La complexation de ces groupements internes par [AuCl(tht)] permet de greffer régiosélectivement jusqu'à 90 atomes d'or dans différentes couches. La structure par diffraction de rayons X d'un complexe dinucléaire de première génération est décrite.*

Table 1. ^{31}P NMR data for compounds **5**, **6**, **10**, **11**, **12**, and **13**. Numbering scheme for compounds **3**–**13**.



5 $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.1$ (brs, P_0), 13.5 (d, $^2J(P''_0,P_1) = 31$ Hz, P''_0), 52.6 (d, $^2J(P_1,P''_0) = 31$ Hz, P_1), 62.7 (s, P_2, P_3)

6 8.4 (brs, P_0), 15.0 (d, $^2J(P''_0,P_1) = 19.4$ Hz, P''_0), 35.7 (d, $^2J(P_1,P''_0) =$ 19.4 Hz, P1), 62.4 (s, P_2), 62.6 (s, P_3)

10 $\delta = -22.8$ (s, P'_1), -12.8 (dd, $^2J(P_1,P'_1) = 59$ Hz, $^2J(P_1,P''_0) = 23$ Hz, P_1), 8.1 (brs, P_0), 13.3 (d, $^2J(P''_0,P_1) = 23$ Hz, P''_0), 46.1 (d, $^2J(P'_1,P_1) = 59$ Hz, P'_1), 62.7 (s, P_2, P_3)

11 $\delta = -15.1$ (dd, $^2J(P_1,P'_1) = 52.0$ Hz, $^2J(P_1,P''_0) = 18.1$ Hz, P_1), 8.4 (s, P_0), 15.2 (d, $^2J(P''_0,P_1) = 18.1$ Hz, P''_0), 21.7 (s, P''_1), 30.7 (d, $^2J(P'_1,P_1) = 52.0$ Hz, P'_1), 62.7 (s, P_2, P_3)

12 $\delta = -12.9$ (brd, P_1), 8.0 (brs, P_0), 13.3 (brs, $^2J(P,P)) = 31$ Hz, P''_0, P''_1, P''_2), 14.3 (d, $^2J(P''_3,P''_4) = 31$ Hz, P''_3), 46.0 (brd, P'_1), 51.3 (d, $^2J(P'_4,P''_3) =$ 31 Hz, P'_4), 52.8 (d, $^2J(P,P) = 31$ Hz, P'_2, P'_3), 62.6 (s, P_2, P_3)

13 $\delta = -15.2$ (brd, $^2J(P_1,P'_1) = 59$ Hz, P_1), 7.6 (brs, P_0), 14.6 (brd, $^2J(P,P) = 17.7$ Hz, P''_0, P''_1, P''_2), 15.6 (d, $^2J(P''_3,P'_4 = 19.1$ Hz, P''_3), 30.5 (brd, $^2J(P'_1,P_1) = 59$ Hz, P'_1), 34.1 (m, P'_2, P'_3), 35.4 (d, $^2J(P'_4,P''_3) =$ 19.1 Hz, P'_4), 62.2 (s, P_2, P_3)

A post-modification at the level of generation 1 in dendrimer **5** then was performed in order to introduce different ligands which are also able to coordinate gold. The strategy shown in Scheme 3 was used to incorporate six P=N–P=N–P=S linkages and twelve internal phosphino groups. The resulting dendrimer **10** (Table 1) (1 equiv) was reacted with eighteen equivalents of [AuCl(tht)]: gold complexation took place cleanly to give the metalladendrimer **11** with eighteen internal AuCl units (P=N–P=N–P=S →AuCl and CH_2PPh_2 →AuCl). Once again, complexation can be followed unambiguously by ^{31}P NMR.[6]

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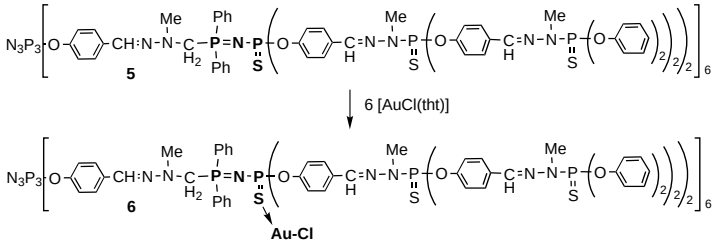
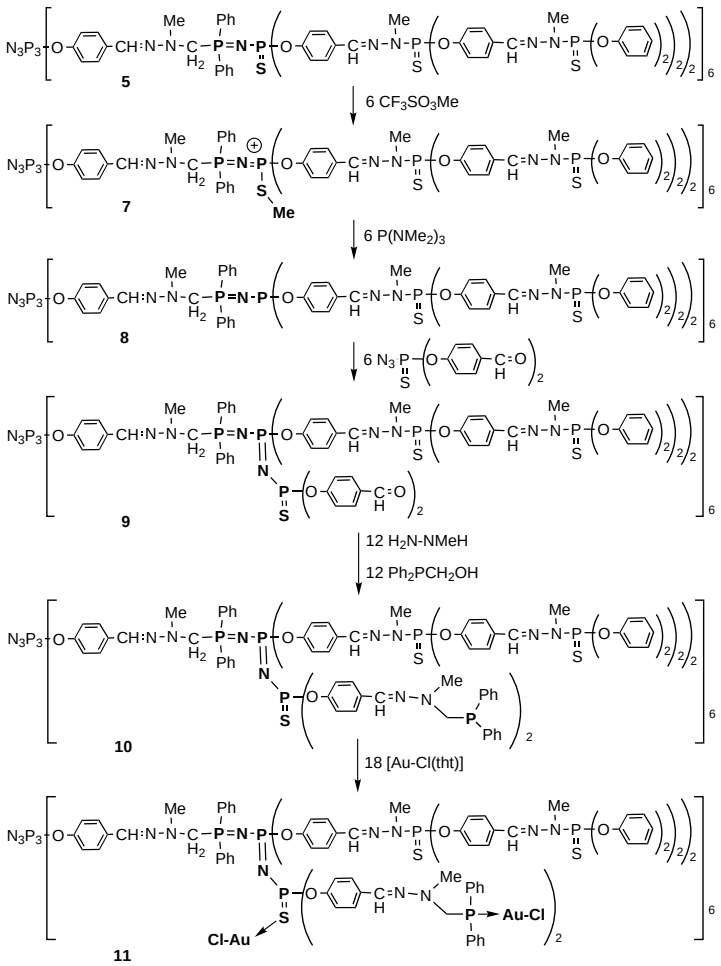


Scheme 2. Synthesis of the hexanuclear gold complex dendrimer **6**.

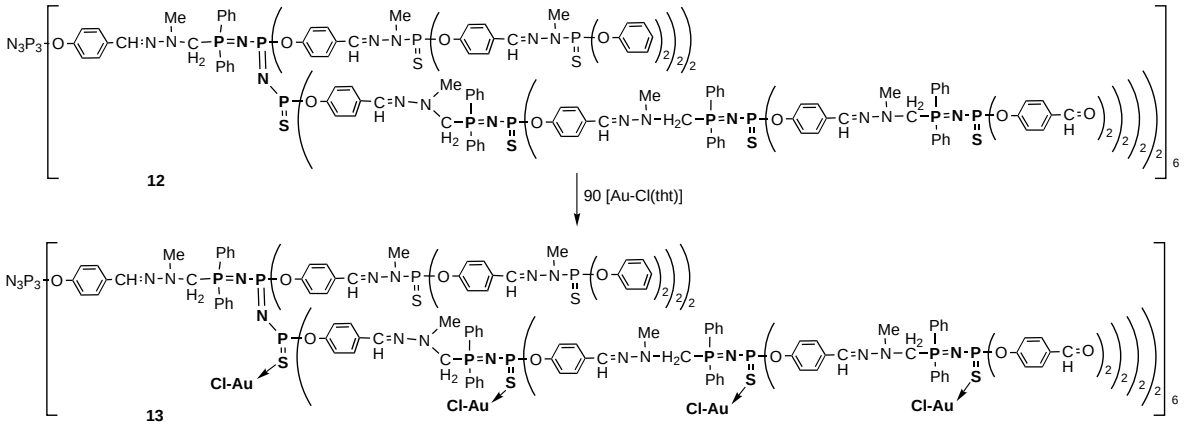


Scheme 3. Incorporation of 18 Au–Cl moieties through complexation of CH_2PPh_2 and P=N–P=N–P=S groups.

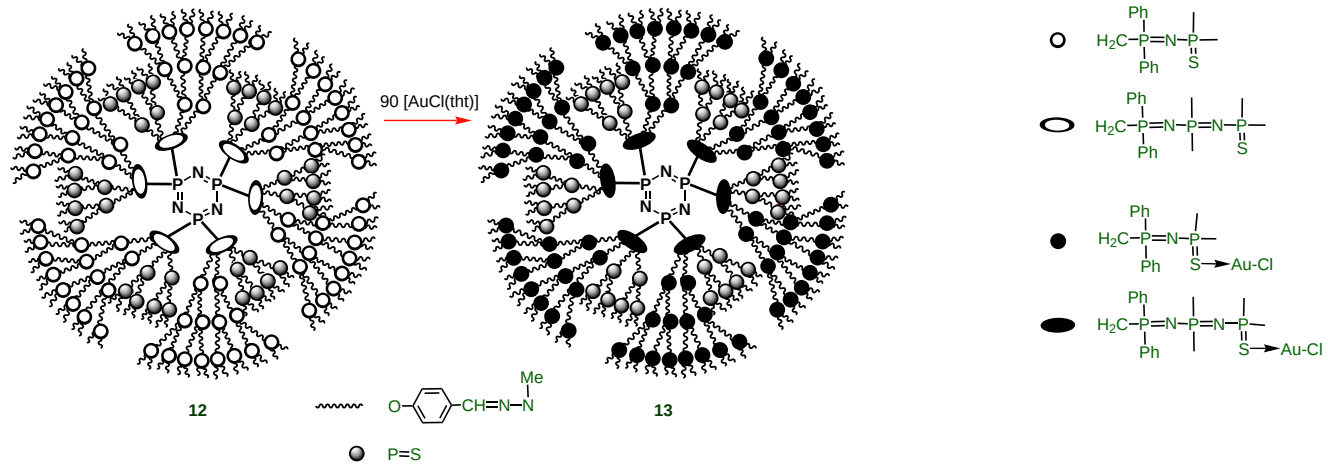
A controlled polydendritic structure, such as **12** (Table 1, Scheme 4), formed by the regioselective stepwise growth of six dendrimer units within the cascade structure of a main dendrimer,[5] appeared to be a model of choice to demonstrate that it is possible to graft up to 90 AuCl units selectively onto different internal layers and that it is also possible to prepare multidendritic systems incorporating both complexed and noncomplexed dendritic moieties. Dendrimer **12**[6] contains a main dendrimer of generation 3 in which each monomer constituting the framework of the macromolecule does not contain any ligand able to complex gold, as well as six dendrimer units, also of generation 3, each of which bears P=N–P=S groups at each generation. Moreover, the branching points between the main dendrimer and the six others are made up of P=N–P=N–P=S units. Therefore, each of the six internal dendrimers possesses a P=N–P=N–P=S linkage at the focal point and two, four, and eight P=N–P=S groups on generation 1, 2, and 3, respectively. A clean reaction occurs when **12** (1 equiv) is treated with [AuCl(tht)] (90 equiv) to give the complex **13** (Table 1), which bears gold only within the cascade structure of the six internal dendrimers (Schemes 4 and 5). As shown in Figure 2, the reaction can be monitored by ^{31}P NMR, which clearly shows that selective complexation of gold has occurred.

Conclusion

In summary, we have demonstrated that incorporation of gold selectively in particular internal layers of dendritic and polydendritic macromolecules can be simply performed by complexation of internal P=N–P=N–P=S or P=N–P=S units. Extension of this methodology to the incorporation of various other metals within the cascade structure as well as to the filling of each generation with different metals is underway.



Scheme 4. Incorporation of 90 Au–Cl moieties into the multidendritic system **12** through complexation with P=N–P=S groups.



Scheme 5. Selective complexation of Au–Cl by the multidendritic macromolecule **12**.

Experimental Section

General: All manipulations were carried out with standard high-vacuum techniques and under an atmosphere of dry argon. ^{31}P NMR spectra were recorded relative to 85% H_3PO_4. See Table 1 and Figure 3 for the numbering scheme used for NMR. $N_3P(S)(OC_6H_4CHO)_2$,[4] Ph_2PCH_2OH,[8] and [AuCl(tht)][9] were synthesized according to published procedures.

Synthesis of dendrimer 9: A solution of $N_3P(S)(OC_6H_4CHO)_2$ (143 mg, 412 mmol) at room temperature was added to a solution of the dendrimer **8** (1000 mg, 0.068 mmol), which possesses internal aminophosphite functions, in THF (10 mL). Evolution of nitrogen occurred rapidly. The solution was stirred for 2 h and the solvent evaporated. The residue was washed with ether (20 mL) and then pentane (20 mL) to give **9** (96% yield) as a white powder.

Synthesis of dendrimer 10: To a solution of dendrimer **9** (1000 mg, 0.060 mmol) in THF (10 mL) was added a slight excess of methylhydrazine (77 µL, 1.456 mmol) in the presence of a molecular sieve (4 Å). The solution was stirred for 24 h at room temperature. After filtration, the resulting solution was evaporated to dryness and the residue was washed with ether (25 mL) to give the dendrimer, which contains terminal HC=N–NHCH$_3$ groups, as a white powder. This dendrimer was dissolved in THF (15 mL) and added to a solution of the phosphine Ph_2PCH_2OH (157 mg, 728 mmol) in THF (10 mL). The resulting mixture was stirred for 2 h, then the solvent was evaporated. The resulting paste was washed with

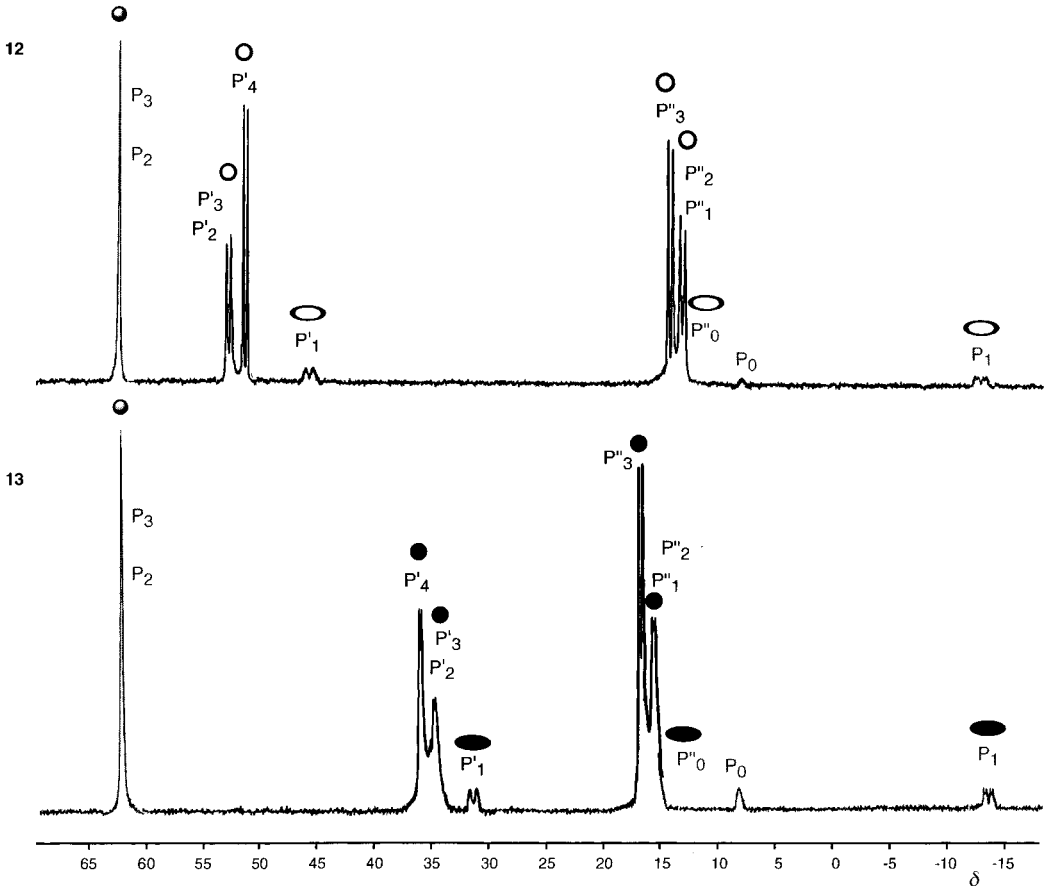


Figure 2. ^{31}P NMR spectra of dendrimer **12** and of dendrimer **13**. The key to the markers is given in Scheme 5.

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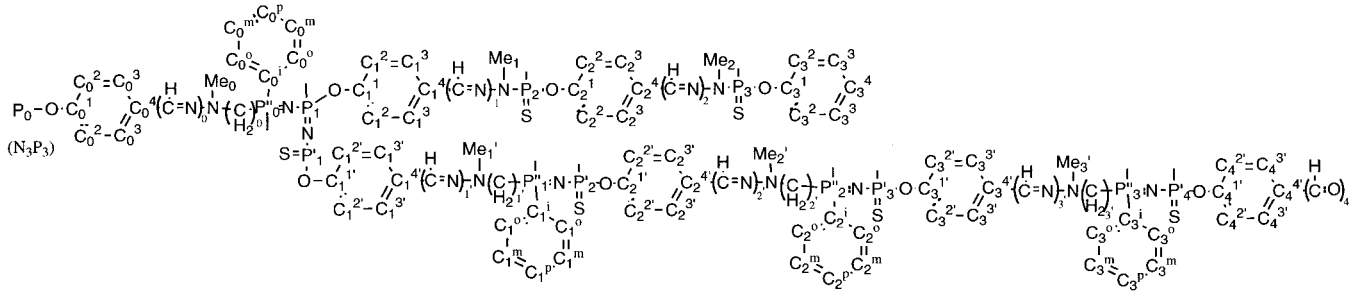

Figure 3.

ether (15 mL) and then with pentane (15 mL) to give **10** (91 % yield) as a white powder.

General procedure for the complexation of dendrimers 3, 5, 10, and 12 with [AuCl(tht)]: To dendrimers **3** (176 mg, 0.101 mmol) or **5** (500 mg, 0.033 mmol) in solution in dichloromethane (10 mL), or to dendrimers **10** (450 mg, 0.023 mmol) or **12** (300 mg, 0.004 mmol) in solution in THF (10 mL) was added three (97 mg, 304 mmol), eight (87 mg, 271 mmol), twenty (150 mg, 469 mmol) or a hundred (154 mg, 481 mmol) equivalents of [AuCl(tht)], respectively, at room temperature. The colorless solution instantaneously turned beige or pale yellow. The mixture was stirred for 2 h, and the solvent was then removed under vacuum. The residue was washed with dichloromethane/pentane (1:5) (2×30 mL) to remove the excess [AuCl(tht)] and gave the dendrimers **4**, **6**, **11**, and **13** in 90 – 97 % yield as beige or pale yellow powders.

Dendrimer 3: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 20.9$ (d, $^2J(P'_0,P_0) = 35.0$ Hz, P'_0), 51.9 (d, $^2J(P_0,P'_0) = 35.0$ Hz, P_0), 62.1 (s, P_1); ^1H NMR ($CDCl_3$): $\delta = 1.15$ (m, 4H, CH_2), 1.42 (m, 4H, CH_2), 2.57 (m, 4H, $(CH_2)^i$), 2.74 (d, $^3J(H,P_1) = 14.2$ Hz, 12H, Me), 7.04 – 7.87 (m, 40H, C_6H_4, C_6H_5, CH=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 22.0$ (d, $^3J(C,P'_0) = 4$ Hz, $(CH_2)^3$), 26.6 (d, $^1J(C,P'_0) = 63$ Hz, $(CH_2)^1$), 30.5 (d, $^2J(C,P'_0) = 16$ Hz, $(CH_2)^2$), 31.8 (d, $^2J(C,P_1) = 12$ Hz, Me), 123.1 (d, $^3J(C,P_0) = 6$ Hz, C_0^2), 129.4 (d, $^3J(C,P'_0) = 14$ Hz, C_0^m), 129.1 (s, C_3^3), 132.1 (d, $^2J(C,P'_0) = 11$ Hz, C_0^o), 132.8 (s, C_0^p), 132.8 (s, C_0^4), 142.1 (d, $^3J(C,P_1) = 19$ Hz, $(CH{=}N)_0$), 154.6 (d, $^2J(C,P_0) = 8$ Hz, C_0^1), (C_0^i not detected); IR (KBr): $\tilde{\nu} = 1602\ cm^{-1}$ (C=N); $C_{62}H_{64}N_{10}O_4P_8S_6Cl_8$ (1737.1): C 42.87, H 3.71, N 8.06; found: C 42.68, H 3.57, N 7.97.

Dendrimer 4: Yield: 97 %; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 22.6$ (d, $^2J(P'_0,P_0) = 27.4$ Hz, P'_0), 34.9 (d, $^2J(P_0,P'_0) = 27.4$ Hz, P_0), 62.1 (s, P_1); ^1H NMR ($CDCl_3$): $\delta = 1.43$ (m, 8H, CH_2), 2.79 (m, 4H, CH_2), 3.47 (d, $^3J(H,P) = 13.95$ Hz, 12H, Me), 7.17 – 7.70 (m, 4H, C_6H_4, C_6H_5, CH=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.2$ (d, $^3J(C,P_0) = 3.1$ Hz, $(CH_2)^3$), 26.9 (dd, $^1J(C,P'_0) = 68.1$ Hz, $^3J(C,P_0) = 3.4$ Hz, $(CH_2)^1$), 29.5 (d, $^2J(C,P_0) = 16.75$ Hz, $(CH_2)^2$), 31.8 (d, $^2J(C,P_1) = 13.3$ Hz, Me), 121.7 (d, $^3J(C,P_0) = 5.1$ Hz, C_0^2), 126.6 (dd, $^1J(C'_1,P'_0) = 108.8$ Hz, $^3J(C'_1,P_0) = 4.8$ Hz, C_1^1), 128.7 (s, C_0^3), 129.1 (d, $^2J(C,P'_0) = 12.8$ Hz, C_0^m), 131.3 (d, $^3J(C,P'_0) = 10.8$ Hz, C_0^o), 133.1 (brs, C_3^3, C_0^p), 140.6 (d, $^3J(C,P_1) = 18.8$ Hz, CH=N), 151.8 (d, $^2J(C,P'_0) = 11.2$ Hz, C_0^1); IR (KBr): $\tilde{\nu} = 335\ cm^{-1}$ (Au–Cl); $C_{62}H_{64}N_{10}O_4P_8S_6Au_2Cl_{10}$ (2202.0): C 33.82, H 2.91, N 6.36; found: C 33.72, H 2.78, N 6.24.

Dendrimer 5: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.1$ (brs, P_0), 13.5 (d, $^2J(P''_0,P_1) = 31$ Hz, P''_0), 52.6 (d, $^2J(P_1,P''_0) = 31$ Hz, P_1), 62.7 (s, P_2, P_3); ^1H NMR ($CDCl_3$): $\delta = 2.77$ (s, 18H, Me_0), 3.27 (m, 108H, Me_1, Me_2), 4.72 (brs, 12H, CH_2), 6.75 – 7.70 (m, 510H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 32.9$ (brd, $^2J(C,P) = 13$ Hz, Me_1, Me_2), 39.0 (s, Me_0), 56.8 (brd, $^1J(C,P''_0) = 73$ Hz, CH_2), 120.5 (s, C_0^2), 121.2 (d, $^3J(C,P_3) = 4$ Hz, C_3^3), 121.7 (brs, C_1^2, C_2^2), 125.2 (s, C_3^4), 126.5 (s, C_0^3), 127.7 (dd, $^1J(C,P'_0) = 109$ Hz, $^3J(C,P_1) = 6$ Hz C_1^1), 127.9 (s, C_1^3), 128.1 (s, C_2^3), 128.4 (d, $^3J(C,P'_0) = 12$ Hz, C_0^m), 129.4 (s, C_3^3), 130.8 (s, C_1^4 and $(HC{=}N)_0$), 132.0 (d, $^2J(C,P'_0) = 10$ Hz, C_0^o), 132.1 (s, C_2^4), 132.4 (s, C_0^p), 133.2 (s, C_0^4), 138.4 (d, $^3J(C,P_3) = 13$ Hz, $(HC{=}N)_2$), 139.4 (d, $^3J(C,P_2) = 13$ Hz, $(HC{=}N)_1$), 149.6 (brs, C_0^1), 150.4 (d, $^2J(C,P_3) = 7$ Hz, C_3^1), 151.1 (d, $^2J(C,P_2) = 7$ Hz, C_2^1), 152.7 (d, $^2J(C,P_1) = 9$ Hz, C_1^1); $C_{702}H_{648}N_{93}O_{90}P_{51}S_{42}$ (14754): C 57.15, H 4.43, N 8.83; found: C 56.98, H 4.40, N 8.74.

Dendrimer 6: Yield: 96 %; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.4$ (s, P_0), 15.0 (d, $^2J(P''_0,P_1) = 19.4$ Hz, P''_0), 35.7 (d, $^2J(P_1,P''_0) = 16.9$ Hz, P_1), 62.4 (s, P_2), 62.6 (s, P_3); ^1H NMR ($CDCl_3$): $\delta = 2.76$ (s, 18H, Me_0), 3.27 (m, 108H, Me_1, Me_2), 4.78 (m, 12H, CH_2), 6.80 – 7.70 (m, 510H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 32.9$ (brd, $^2J(C,P) = 12.8$ Hz, Me_1, Me_2), 39.4 (brs, Me_0), 57.5 (brd, $^1J(C,P''_0) = 67.0$ Hz, CH_2), 120.5 (s, C_0^2), 121.2 (d, $^3J(C,P_3) = 3.6$ Hz, C_3^3), 121.6 (brs, C_1^2, C_2^2), 125.3 (s, C_3^4), 126.8 (s, C_0^3), 128.2 (brs, C_1^3, C_2^3), 128.8 (d, $^3J(C,P''_0) = 12.2$ Hz, C_0^m), 129.4 (s, C_3^3), 130.0 (brs, C_0^4), 131.2 (s, $(HC{=}N)_0$), 132.1 (s, C_2^4), 132.2 (d, $^2J(C,P''_0) = 8.45$ Hz, C_0^o), 132.9 (s, C_1^4), 133.3 (s, C_0^p), 138.5 (d, $^3J(C,P_2) = {}^3J(C,P_3) = 14$ Hz, $(HC{=}N)_1$, $(HC{=}N)_2$), 149.7 (d, $^2J(C,P_0) = 7.2$ Hz, C_0^1), 150.4 (d, $^2J(C,P_3) = 7.3$ Hz, C_3^1), 151.1 (d, $^2J(C,P_2) = 6.0$ Hz, C_2^1), 151.2 (d, $^2J(C,P_1) = 7.3$ Hz, C_1^1); IR (KBr) $\tilde{\nu} = 315\ cm^{-1}$ (Au–Cl); $C_{702}H_{648}N_{93}O_{90}P_{51}S_{42}Au_6Cl_6$ (16149): C 54.07, H 4.16, N 8.36; found: C 53.78, H 3.88, N 8.17.

Dendrimer 9: $^{31}P\{^1H\}$ NMR (CDCl3): $\delta = -12.4$ (dd, $^2J(P_1,P'_1) = 62$ Hz, $^2J(P_1,P''_0) = 21$ Hz, P_1), 8.0 (brs, P_0), 13.4 (d, $^2J(P''_0,P_1) = 21$ Hz, P''_0), 44.7 (d, $^2J(P'_{11},P_1) = 62$ Hz, P'_1), 62.6 (s, P_2), 62.7 (s, P_3); ^1H NMR ($CDCl_3$): $\delta = 2.71$ (s, 18H, Me_0), 3.30 (m, 108H, Me_1, Me_2), 4.60 (brs, 12H, CH_2), 6.80 – 7.70 (m, 558H, C_6H_5, C_6H_4, HC=N), 9.73 (s, 12H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 32.9$ (d, $^2J(C,P) = 13$ Hz, Me_1, Me_2), 39.0 (s, Me_0), 58.7 (d, $^1J(C,P''_0) = 78$ Hz, CH_2), 120.5 (s, C_0^2), 121.2 (d, $^3J(C,P_3) = 4$ Hz, C_3^2), 121.6 (brs, C_1^2, C_2^2, $C_1^{2'}$), 125.3 (s, C_3^4), 126.6 (s, C_0^3), 126.9 (d, $^1J(C,P_0) = 103$ Hz, C_0^1), 128.0 (s, C_3^3), 128.1 (s, C_2^3), 128.6 (d, $^3J(C,P''_0) = 12$ Hz, C_0^m), 129.4 (s, C_3^3), 130.9 (s, C_1^4, $(HC{=}N)_0$, $C_1^{3'}$), 132.1 (d, $^2J(C,P''_0) = 7$ Hz, C_0^o), 132.2 (s, C_2^4, $C_1^{4'}$, C_0^p), 132.8 (s, C_0^4), 138.4 (d, $^3J(C,P_3) = 14$ Hz, $(HC{=}N)_2$), 138.9 (d, $^3J(C,P_2) = 13$ Hz, $(HC{=}N)_1$), 149.8 (s, C_0^1), 150.4 (d, $^2J(C,P_3) = 7$ Hz, C_3^1), 151.1 (d, $^2J(C,P_2) = 7$ Hz, C_2^1), 151.9 (d, $^2J(C,P_1) = 9$ Hz, C_1^1), 156.5 (d, $^2J(C,P'_1) = 9$ Hz, $C_1^{1'}$), 190.9 (s, CHO); IR (KBr): $\tilde{\nu} = 1700\ cm^{-1}$ (C=O); $C_{786}H_{708}N_{99}O_{114}P_{57}S_{42}$ (16478): C, 57.29; H, 4.33; N, 8.42; found: C, 57.11; H, 4.28; N, 8.27.

Dendrimer 10: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -22.8$ (s, P''_1), -12.8 (dd, $^2J(P_1,P'_1) = 59$ Hz, $^2J(P_1,P''_0) = 23$ Hz, P_1), 8.1 (brs, P_0), 13.3 (d, $^2J(P''_0,P_1) = 23$ Hz, P''_0), 46.1 (d, $^2J(P'_1,P_1) = 59$ Hz, P'_1), 62.7 (s, P_2, P_3); ^1H NMR ($CDCl_3$): $\delta = 2.69$ (s, 18H, Me_0), 2.80 (s, 36H, Me'_1), 3.27 (brs, 108H, Me_1, Me_2), 4.10 (brs, 24H, $(CH_2)'_1$), 4.67 (brs, 12H, $(CH_2)_0$), 6.80 – 7.70 (m, 690H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$): [$(HC{=}N)_0$, $(HC{=}N)'_1$ not detected] $\delta = 32.8$ (d, $^2J(C,P) = 13$ Hz, Me_1, Me_2), 38.8 (s, Me'_1), 38.9 (s, Me_0), 58.6 (d, $^1J(C,P''_0) = 80$ Hz, $(CH_2)_0$), 61.0 (d, $^1J(C,P''_1) = 10$ Hz, $(CH_2)'_1$), 120.4 (s, C_0^2), 121.2 (brs, C_3^2), 121.6 (d, $^3J(C,P) = 3$ Hz, C_1^2, C_2^2, $C_1^{2'}$), 125.2 (s, C_3^4), 126.1 (s, $C_1^{3'}$), 126.4 (s, C_0^3), 126.9 (brd, $^1J(C,P''_0) = 102$ Hz, C_0^1), 127.9 (s, C_1^3), 128.1 (s, C_2^3), 128.3 (d, $^3J(C,P''_1) = 14$ Hz, C_1^m), 128.3 (s, C_1^p), 128.5 (brd, C_0^m), 129.3 (s, C_3^3), 130.9 (s, C_1^4), 131.4 (s, $C_0^{4'}$), 132.1 (s, C_2^4, C_0^o, C_0^p), 132.5 (s, C_0^4), 132.8 (d, $^2J(C,P''_1) = 19$ Hz, C_1^o), 137.6 (d, $^1J(C,P'_1) = 14$ Hz, C_1^1), 138.3 d, $^3J(C,P_3) = 14$ Hz, $(HC{=}N)_2$), 139.2 (d, $^3J(C,P_2) = 13$ Hz, $(HC{=}N)_1$), 149.6 (s, C_0^1), 150.4 (d, $^2J(C,P_3) = 7$ Hz, C_3^1), 151.2 (d, $^2J(C,P) = 7$ Hz, C_2^1, $C_1^{1'}$), 152.1 (d, $^2J(C,P_1) = 8$ Hz, C_1^1); $C_{954}H_{888}N_{123}O_{102}P_{69}S_{42}$ (19193): C 59.70, H 4.66, N 8.97; found: C 59.48, H 4.51, N 9.07.

Dendrimer 11: Yield: 91 % $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -15.1$ (dd, $^2J(P_1,P'_1) = 52.0$ Hz, $^2J(P_1,P''_0) = 18.1$ Hz, P_1), 8.4 (s, P_0), 15.2 (d, $^2J(P''_0,P_1) = 18.1$ Hz, P''_0), 21.7 (s, P''_1), 30.7 (d, $^2J(P'_1,P_1) = 52.0$ Hz, P'_1), 62.7 (s, P_2, P_3); ^1H NMR ($CDCl_3$): $\delta = 2.69$ (brs, 18H, Me_0), 2.81 (brs, 36H, Me'_1), 3.22 (brs, 36H, Me_1), 3.27 (brs, 72H, Me_2), 4.38 (brs, 24H, $(CH_2)'_1$), 4.52 (brs, 12H, $(CH_2)_0$), 6.9 – 7.7 (m, 690H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$): [$(HC{=}N)_0$, $(HC{=}N)'_1$ not detected] $\delta = 32.9$ (d, $^2J(C,P) = 13$ Hz, Me_1, Me_2), 39.1 (s, Me'_1), 39.5 (s, Me_0), 59.3 (m, $(CH_2)_0$, $(CH_2)'_1$), 120.6 (brs, C_0^2), 121.2 (brs, C_3^2), 121.6 (brs, C_1^2, C_2^2, $C_1^{2'}$), 125.2 (s, C_3^4), 126.7 (s, C_0^3), 126.9 (brd, $^1J(C,P''_0) = 102$ Hz, C_0^1), 127.8 (s, C_1^3), 128.2 (s, C_2^3), 129.1 (d, $^3J(C,P''_1) = 11.25$ Hz, C_1^m), 129.4 (brs, C_0^m, C_1^p), 129.5 (brs, C_3^3), 131.7 (m, C_1^4, $C_1^{4'}$), 132 (s, C_2^4, C_0^o, C_0^p), 132.5 (s, C_0^4), 132.6 (d, $^2J(C,P'_1) = 22$ Hz, C_1^o), 138.5 (d, $^2J(C,P'_1) = 13.8$ Hz, C_1^1), 138.5 (d, $^3J(C,P_3) = 13.8$ Hz, $(HC{=}N)_2$), 139.4 (d, $^3J(C,P_2) = 10.9$ Hz, $(HC{=}N)_1$), 149.7 (s, C_0^1), 149.9 (d, $^2J(C,P_3) = 7$ Hz, C_3^1), 150.4 (d, $^2J(C,P) = 7$ Hz, C_2^1, $C_1^{1'}$), 152.5 (d, $^2J(C,P) = 7.9$ Hz, C_1^1);

$C_{954}H_{888}N_{123}O_{102}P_{69}S_{42}Au_{18}Cl_{18}$ (23376): C 49.02, H 3.83, N 7.37; found: C 48.81, H 3.67, N 7.25.

Dendrimer 12: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -12.9$ (br d, P_1), 8.0 (br s, P_0), 13.3 (br d, $^2J(P,P) = 31$ Hz, P''_0, P''_1, P''_2), 14.3 (d, $^2J(P''_3,P'_4) = 31$ Hz, P''_3), 46.0 (br d, P'_1), 51.3 (d, $^2J(P'_4,P''_3) = 31$ Hz, P'_4), 52.8 ($^2J(P,P) = 31$ Hz, P'_2, P'_3), 62.6 (s, P_2, P_3); ^1H NMR ($CDCl_3$): $\delta = 2.80$ (s, 270 H, Me_0, Me'_1, Me'_2, Me'_3), 3.18 (br s, 108 H, Me_1, Me_2), 4.73 (br s, 180 H, $(CH_2)_0$, $(CH_2)'_1$, $(CH_2)'_2$, $(CH_2)'_3$), 6.80 – 7.70 (m, 2154 H, C_6H_5, C_6H_4, HC=N), 9.84 (s, 96 H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$): [$(CH_2)_0$, $(CH_2)^i_1$, C^3_0, C^4_0, C^i_0, $(HC{=}N)_0$, $(HC{=}N)'_1$, $(HC{=}N)'_2$, $(HC{=}N)'_3$ not detected] $\delta = 32.8$ (d, $^2J(C,P) = 12$ Hz, Me_1, Me_2), 38.7 (s, Me_0, Me'_1), 38.9 (s, Me'_2), 39.0 (s, Me'_3), 56.7 (d, $^1J(C,P''_3) = 74$ Hz, $(CH_2)''_3$), 56.9 (d, $^1J(C,P''_2) = 70$ Hz, $(CH_2)''_2$), 120.4 (s, C^2_0), 121.2 (br s, C^2_3), 121.4 (br s, C^2_1, C^2_2), 121.9 (br d, $^3J(C,P) = 5$ Hz, $C^{2'}_1$, $C^{2'}_2$, $C^{2'}_3$, $C^{2'}_4$), 125.2 (s, C^3_4), 126.2 (s, $C^{3'}_1$, $C^{3'}_2$, $C^{3'}_3$), 127.6 (dd, $^1J(C,P''_3) = 105$ Hz, $^3J(C,P'_4) = 5$ Hz, C^i_3), 127.9 (s, C^3_1), 128.0 (br d, $^1J(C,P''_2) = 104$ Hz, C^i_2), 128.1 (s, C^3_2), 128.3 (d, $^3J(C,P) = 10$ Hz, C^m_0, C^m_1, C^m_2), 128.5 (d, $^3J(C,P''_3) = 11$ Hz, C^m_3), 131.0 (s, $C^{3'}_4$), 131.1 (s, C^4_1), 131.9 (d, $^2J(C,P) = 9$ Hz, C^o_0, C^o_1, C^o_2, C^o_3), 132 (s, C^p_0, C^p_1, C^p_2, C^p_3), 132.2 (s, C^4_2), 132.5 (s, $C^{4'}_1$, $C^{4'}_2$, $C^{4'}_3$, $C^{4'}_4$), 138.4 (d, $^3J(C,P_3) = 13$ Hz, $(HC{=}N)_2$), 139.1 (br s, $(HC{=}N)_1$), 149.5 (br s, C^1_0), 150.3 (d, $^2J(C,P_3) = 7$ Hz, $C^{1'}_3$), 151.0 (d, $^2J(C,P_2) = 7$ Hz, $C^{1'}_2$), 151.2 (d, $^2J(C,P'_2) = 9$ Hz, $C^{1'}_2$), 151.3 (d, $^2J(C,P'_3) = 9$ Hz, $C^{1'}_3$), 151.4 (br s, $C^{1'}_1$), 152.2 (br s, C^1_1), 156.5 (d, $^2J(C,P'_4) = 9$ Hz, $C^{1'}_4$), 190.9 (s, CHO); IR (KBr): $\tilde{\nu} = 1699\ cm^{-1}$ (C=O); $C_{3138}H_{2808}N_{352}O_{366}P_{225}S_{126}$ (62304): C 60.49, H 4.54, N 7.89; found: C 60.21, H 4.41, N 7.75.

Dendrimer 13: Yield: 97% $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -15.2$ (br d, $^2J(P_1,P'_1) = 59$ Hz, P_1), 7.6 (br s, P_0), 14.6 (br d, $^2J(P,P) = 17.7$ Hz, P''_0, P''_1, P''_2), 15.6 (d, $^2J(P''_3,P'_4) = 19.1$ Hz, P''_3), 30.5 (br d, $^2J(P'_1,P_1) = 59$ Hz, P'_1), 34.1 (m, P'_2, P'_3), 35.4 (d, $^2J(P'_4,P''_3) = 19.1$ Hz, P'_4), 62.2 (s, P_2, P_3); ^1H NMR ($CDCl_3$): $\delta = 2.83$ (s, 270 H, Me_0, Me'_1, Me'_2, Me'_3), 3.35 (br s, 108 H, Me_1, Me_2), 4.76 (br s, 180 H, $(CH_2)_0$, $(CH_2)'_1$, $(CH_2)'_2$, $(CH_2)'_3$), 6.90 – 7.80 (m, 2154 H, C_6H_5, C_6H_4, HC=N), 9.86 (s, 96 H, CHO); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): [$(CH_2)_0$, $(CH_2)^i_1$, C^3_0, C^4_0, C^i_0, $(HC{=}N)_0$, $(HC{=}N)'_1$, $(HC{=}N)'_2$, $(HC{=}N)'_3$ not detected] $\delta = 33.2$ (d, $^2J(C,P) = 12.4$ Hz, Me_1, Me_2), 39.5 (s, Me_0, Me'_1), 40.2 (s, Me'_2, Me'_3), 57.7 (br d, $^1J(C,P) = 76$ Hz, $(CH_2)'_2$, $(CH_2)'_3$), 120.9 (s, C^2_0), 121.4 (br s, C^2_3), 121.9 (s, C^2_1, C^2_2), 122.1 (br d, $^3J(C,P) = 4.4$ Hz, $C^{2'}_1$, $C^{2'}_2$, $C^{2'}_3$, $C^{2'}_4$), 125.3 (s, C^4_3), 126.3 (s, $C^{3'}_1$, $C^{3'}_2$, $C^{3'}_3$), 127.6 (dd, $^1J(C,P''_3) = 94$ Hz, $^3J(C,P'_4) = 5$ Hz, C^i_3), 128.7 (s, C^3_1), 128.9 (d, $^1J(C,P''_2) = 94$ Hz, C^i_2), 129.2 (br d, $^3J(C,P) = 10.6$ Hz, C^m_0, C^m_1, C^m_2), 129.3 (d, $^3J(C,P''_3) = 12.1$ Hz, C^m_3), 129.7 (s, $C^{3'}_4$), 131 (s, C^4_1), 131.5 (s, C^4_2, C^4_2), 132.3 (d, $^2J(C,P) = 10.7$ Hz, C^o_0, C^o_1, C^o_2, C^o_3), 132.5 (s, C^p_0, C^p_1, C^p_2, C^p_3), 133.8 (s, C^4_2), 134.0 (br s, $C^{4'}_1$, $C^{4'}_3$), 139.2 (br d, $^3J(C,P_3) = 14$ Hz, $(HC{=}N)_2$), 139.8 (br s, $(HC{=}N)_1$), 150.2 (br d, $^2J(C,P) = 9.0$ Hz, C'_2, C'_3, C''_3), 150.7 (d, $^2J(C^{1'}_2,P'_1) = 6.7$ Hz, $C^{1'}_2$), 151.4 (d, $^2J(C^{1'}_1,P'_1) = 8.0$ Hz, $C^{1'}_1$), 151.8 (br d, $^2J(C,P) = 7.4$ Hz, $C^{1'}_0$, $C^{1'}_1$), 155.1 (d, $^2J(C,P'_4) = 9.7$ Hz, $C^{1'}_4$), 190.8 (s, CHO); IR (KBr) $\tilde{\nu} = 348\ cm^{-1}$ (AuCl); $C_{3138}H_{2802}N_{357}O_{366}P_{225}S_{126}Au_{90}Cl_{90}$ (83216): C 45.29, H 3.39, N 5.91; found: C 45.35, H 3.29, N 5.85.

X-ray data of $C_{62}H_{64}N_{10}O_4P_8S_6Cl_{10}Au_2 \cdot 4CH_2Cl_2$ ($4 \cdot 4CH_2Cl_2$): The structure was determined from a triclinic crystal of dimensions ($0.52 \times 0.40 \times 0.30$) mm (space group $P\bar{1}$), with unit cell $a = 11.175(2)$ Å, $b = 13.274(2)$ Å, $c = 17.157(3)$ Å, $\alpha = 103.24(2)^\circ$, $\beta = 96.57(2)^\circ$, $\gamma = 96.91(2)^\circ$, $V = 2371.8$ Å^3, $Z = 1$, $\rho_{calcd} = 1.73\ g\,cm^{-3}$, $\mu = 38.05\ cm^{-1}$, $F000 = 1249$. A total of 18886 reflections were measured (7020 independent) with $R_{av} = 0.06$. X-ray diffraction analysis of $C_{62}H_{64}N_{10}O_4P_8S_6Cl_{10}Au_2 \cdot 4CH_2Cl_2$ was carried out on a STOE – IPDS (imaging plate detector system) with $Mo_{K\alpha}$ radiation and equipped with an Oxford Cryosystems cooler device. The structure was solved by direct methods (SIR 92) and refined by least-squares procedures on F_{obs}. Hydrogen atoms were located on a difference Fourier map, but they were introduced in the calculation in idealized positions ($d_{C-H} = 0.96$ Å); their atomic coordinates were recalculated after each cycle of refinement. They were given isotropic thermal parameters 20% higher than those of the C atom to which they are referred. All non-hydrogen atoms were anisotropically refined. Least-squares refinements were carried out by minimizing the function $\Sigma w(||F_o| - |F_c||)^2$, where F_o and F_c are the observed and calculated structures. A weighting scheme was used. The model reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $Rw = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w(|F_o|)^2]^{1/2}$.
The final R (Rw) values were 0.038 (0.043) for 5821 reflections ($I > 3\sigma(I)$) and 515 variables. The calculations were carried out with the aid of the PC program CRYSTALS. The molecule was drawn with CAMERON (thermal ellipsoids at the 50% probability level). The atomic structure factors were taken from international tables for X-ray crystallography. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101251. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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