Dendrimer Surface Chemistry. Facile Route to Polyphosphines and Their Gold Complexes

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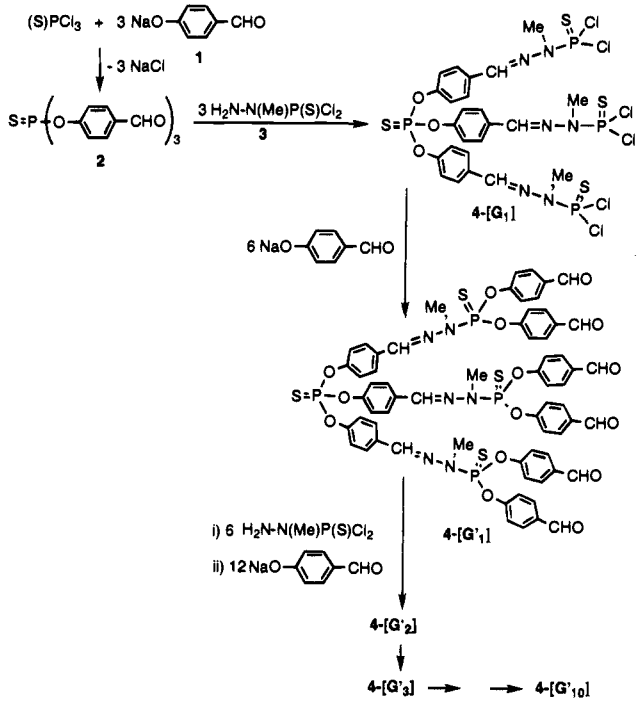
Dendrimers[1]—spherical polymers with a regular and highly symmetrical structure—offer a wide range of unusual physical and chemical properties mainly due to the presence of internal cavities (guest−host systems) and a defined number of functional end groups.[1c,2] We recently reported the preparation of phosphorus-containing dendrimers built up to the seventh generation and possessing two of the most reactive functions in organic and main group element chemistry, aldehyde groups and P−Cl bonds, respectively[3] (Scheme 1).

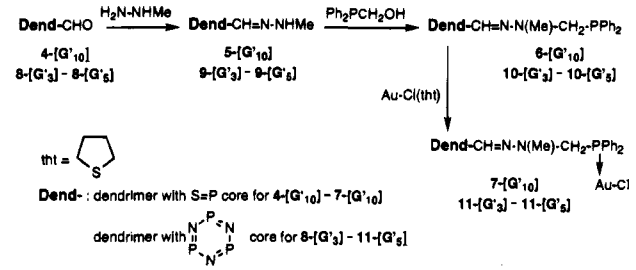
At this stage two main challenges appeared to us important to take up. The first one was to check if steric considerations that dictate the globular shape of these species do not affect the reactivity of the surface functionalities; the second one consisted in the easy and quantitative grafting at the periphery of our P^V dendrimers of a large number of terminal P^{III} phosphino groups.[4] The presence of phosphino end groups would allow the surface of dendrimers to be covered with various metal fragments via complexation and might open, for example, new possibilities in catalysis. We report here the preparation of dendrimers containing up to the theoretically predicted 3072 terminal free phosphino groups and their complexation with gold derivatives. To our knowledge these macromolecules are the largest polyphosphines and the largest polyphosphine complexes of well-defined structure reported until now.

The dendrimer **4-[G′$_{10}$]** (generation 10, 3072 terminal aldehyde groups, theoretical molecular weight 1 020 302) was prepared using the strategy outlined in Scheme 1. Addition of methylhydrazine gave rise quantitatively to **5-[G′$_{10}$]** possessing

Scheme 1



Scheme 2



hydrazono CH=NNH(CH$_3$) end groups, which can be reacted easily with the phosphine Ph_2PCH_2OH to give **6-[G′$_{10}$]**, a compound having 3072 phosphino groups[5] (Scheme 2). Reactions can be followed by NMR (transformation **4-[G′$_{10}$]** → **5-[G′$_{10}$]**, disappearance of signals due to CHO groups and appearance of a singlet for NCH$_3$ groups in ^{1}H and ^{13}C NMR, deshielding of 2.4 ppm for the signal due to P(S) groups closest to the surface in ^{31}P NMR; transformation **5-[G′$_{10}$]** → **6-[G′$_{10}$]**, appearance of doublets for N(CH$_3$) groups in ^{1}H and ^{13}C NMR and of a new signal at −23.5 ppm characteristic of a NCH_2-PPh_2 fragment in ^{31}P NMR). Complexation of the polyphos-

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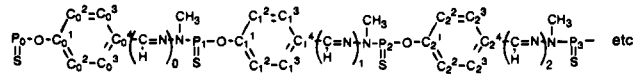
(1) Reviews: (a) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (b) Mekelburger, H. B.; Jaworek, W.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1571. (c) Tomalia, D. A.; Durst, H. D. In *Topics in Current Chemistry, Vol. 165*; *Supramolecular Chemistry 1: Directed Synthesis and Molecular Recognition*; Weber, E., Ed.; Springer-Verlag: Berlin, Heidelberg, 1993; pp 193−313. (d) Ottaviani, M. F.; Bossmann, S.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 661. (e) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (f) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem.* **1994**, *106*, 2507; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413. (g) Moorefield, C. N.; Newkome, G. R. In *Advances in Dendritic Molecules*; Newkome, G. R., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, p 1.

(2) (a) See, for example: Mourey, T. H. *Macromolecules* **1992**, *25*, 2401. (b) Gitsov, I.; Wooley, K. L.; Hawker, J.; Ivanova, P. T.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 5621. (c) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226. (d) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659.

(3) (a) Launay, N.; Caminade, A.-M.; Lahana, R.; Majoral, J.-P. *Angew Chem., Int. Ed. Engl.* **1994**, *33*, 1589. (b) Launay, N.; Caminade, A.-M.; Majoral, J.-P. *J. Am. Chem. Soc.* **1995**, *117*, 3282.

(4) Only a few small organophosphine dendrimers containing up to fifteen P^{III} atoms, eight of them being located at the periphery, were already reported. Their palladium complexes catalyzed the electrochemical reduction of CO_2 to CO. Miedaner, A.; Curtis, C. J.; Barkley, R. M.; DuBois, D. L. *Inorg. Chem.* **1994**, *33*, 5482. Herring, A. M.; Steffey, B. D.; Miedaner, A.; Wander, S. A.; DuBois, D. L. *Inorg. Chem.* **1995**, *34*, 1100.

(5) Selected spectroscopic data for **6-[G′$_{10}$]**. The numbering used for ^{13}C and ^{31}P NMR is as follows:



6-[G′$_{10}$]: white powder; 92% yield; ^{31}P{^{1}H} NMR ($CDCl_3$) δ −22.8 (s, PPh_2), 61.5−62.0 (br s, P_1−P_{10}) ppm; ^{1}H NMR ($CDCl_3$) δ 2.8 (s, 9216 H, $CH_2N(CH_3)$), 3.3 (m, 9207 H, $P_{1,2,3,4,5,6,7,8,9,10}NCH_3$), 4.1 (br s, 6144 H, CH_2P), 7.2−7.7 (m, 58 353 H, C_6H_4, and CH=N); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 32.8 (d, $^2J_{CP1,2,3,4,5,6,7,8,9,10}$ = 13.1 Hz, $P_{1,2,3,4,5,6,7,8,9,10}NCH_3$), 39.0 (d, $^3J_{CP}$ = 6.5 Hz, $N(CH_3)CH_2PPh_2$), 60.8 (d, $^1J_{CP}$ = 11 Hz, CH_2PPh_2), 121.2 (br s, C_{10}^2), 121.7 (br s, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2, C_7^2, C_8^2, C_9^2), 126.4 (s, C_0^3, C_f^3, C_2^3, C_3^3, C_4^3, C_5^3, C_6^3, C_7^3, C_8^3, C_9^3, and C_{10}^3), 128.3 (d, $^3J_{CP}$ = 6.5 Hz, *m*-$(C_6H_5)_2P$), 128.6 (s, *p*-$(C_6H_5)_2P$), 130.5 (s, C_{10}^4), 131.3 (s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4, C_6^4, C_7^4, C_8^4, and C_9^4), 132.9 (d, $^2J_{CP}$ = 18 Hz, *o*-$(C_6H_5)_2P$), 134.0 (s, CH=$NNCH_2$), 137.4 (d, $^1J_{CP}$ = 13 Hz, *i*-$(C_6H_5)_2P$), 139 (m, $(CH{=}N)_{0,1,2,3,4,5,6,7,8,9}$), 150.1 (d, $^2J_{CP}$ = 7 Hz, C_{10}^1), 151.4 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1, C_6^1, C_7^1, C_8^1, C_9^1, and C_{10}^1). **7-[G′$_{10}$]**: white powder; 94% yield; ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 23.7 (s, PPh_2), 64.3 (br s, P_1−P_{10}) ppm; ^{1}H NMR and ^{13}C NMR ($CDCl_3$) data identical to those of **6-[G′$_{10}$]**.

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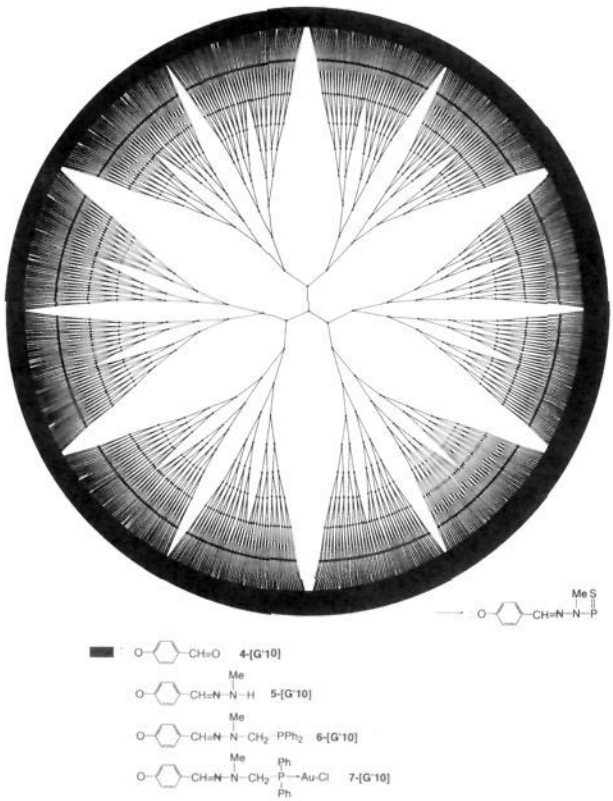

Figure 1.

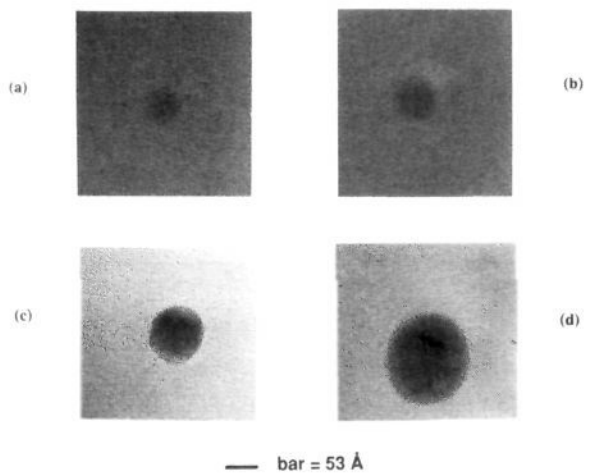

Figure 2. High-resolution transmission electron micrograph of (a) **11-[G′3]**, (b) **11-[G′4]**, (c) **11-[G′5]**, and (d) **7-[G′10]**: 1900K magnification; 300 kV accelerating voltage; reproduced at 45% of original size.

phine **6-[G′10]** (theoretical molecular weight 1 715 385) with AuCl (tetrahydrothiophene)[6] afforded the corresponding dendrimer **7-[G′10]** (white powder), in which the surface is covered theoretically by the 3072 AuCl moieties (Figure 1).[7] The reaction was monitored by ^{31}P NMR, which shows a singlet for the $NCH_2P(Ph)_2$ (AuCl) linkage at +23.7 ppm ($\Delta\delta = 47.2$ ppm).

(6) Uson, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85.

(7) Structure defects cannot be totally ruled out in the limit of ^{31}P NMR precision (1%); therefore the number of terminal phosphino groups or the number of AuCl units is quite likely close to 3000.

The same multistep procedure used for the formation of **4-[G′10]** was applied to the preparation of the new dendrimers **8-[G′1]**−**8-[G′5]** starting from the hexapodant core $N_3P_3Cl_6$ instead of $SPCl_3$. These species were also submitted to treatment with methylhydrazine and then with the phosphine Ph_2PCH_2OH, allowing the formation of the polyphosphines **10-[G′1]**, **10-[G′2]**, **10-[G′3]**, **10-[G′4]**, and **10-[G′5]** possessing 12, 24, 48, 96, and 192 terminal phosphino groups, respectively. Complexation of the last three compounds with AuCl (tetrahydrothiophene) afforded complexes **11-[G′3]**, **11-[G′4]**, and **11-[G′5]** isolated as white stable solids (Scheme 2).

Gold complexes **11-[G′3]**, **11-[G′4]**, **11-[G′5]**, and **7-[G′10]** were imaged by high-resolution electron microscopy in order to compare the size of consecutive generations and to see if higher order structures are formed. Isolated spheres with measured diameters of 60 ± 5 (**11-[G′3]**), 75 ± 5 (**11-[G′4]**), 90 ± 5 (**11-[G′5]**), and 150 ± 5 Å (**7-[G′10]**) were observed (Figure 2).[8] Besides these isolated spheres, aggregates generally adopting a spherical shape were detected with sizes up to 10 000 Å.[9]

In conclusion, such easy reactions to work with led to a variety of dendrimers possessing up to 3072 CH_2PPh_2 or CH_2-PPh_2−AuCl end groups, four of which were directly visualized by HRTEM. No marked difference of chemical reactivity was observed when moving either from dendrimer of the first generation **4-[G′1]** to the dendrimer of the tenth generation **4-[G′10]** or from **8-[G′1]** to **8-[G′5]**. Therefore the shape and the size of these dendritic molecules did not play a decisive role, and surface functionalities always remained available for further reactions. Preliminary experiments showed that complexation of phosphino groups readily occurred also with $Fe_2(CO)_9$ or $W(CO)_5$ THF.

In view of the widespread use of phosphines in coordination chemistry, this easy access to polyphosphines should open new perspectives. Indeed, the preparation of various other dendrimer complexes and their use in catalysis are underway.

Acknowledgment. Thanks are due to the CNRS for financial support, to the EC for a grant (M.S.), and to Ministerio de Educacion y Ciencia (Spain) for a grant (M.B.).

Supporting Information Available: Full experimental details, spectra data, and elemental analysis for products **4-[G′10]**, **5-[G′10]**, **10-[G′1]**−**10-[G′5]**, and **11-[G′3]**−**11-[G′5]** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(8) The length of the repetitive branch $POC_6H_4CH{=}NN(CH_3)P$ was found to be 9.5 Å in **4-[G1]**, which agrees remarkably well with the observed dendrimer size (X-ray crystallographic data): Lartigue, M. L.; Caminade, A.-M.; Majoral, J.-P. Unpublished results.

(9) Electron micrographs of single organic dendrimer molecules[10] or of their aggregates[11] were already reported.

(10) See, for example: (a) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 1, 117. (b) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *9*, 2466. (c) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176. (d) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Behera, R. K.; Escamillia, G. H.; Saunders, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 917.

(11) (a) Newkome, G. R.; Yao, Z. Q.; Baker, G. R.; Gupta, V. K.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849. (b) Newkome, G. R.; Baker, G. R.; Arai, S.; Saunders, M. J.; Russo, P. S.; Theriot, K. J.; Moorefield, C. N.; Rogers, L. E.; Miller, J. E.; Lieux, T. R.; Murray, M. E.; Phillips, B.; Pascal, L. *J. Am. Chem. Soc.* **1990**, *112*, 8458. (c) Newkome, G. R.; Hu, Y.; Saunders, M. J.; Fronczek, F. R. *Tetrahedron Lett.* **1991**, *32*, 1133.