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Specific Functionalization on the Surface of Dendrimers

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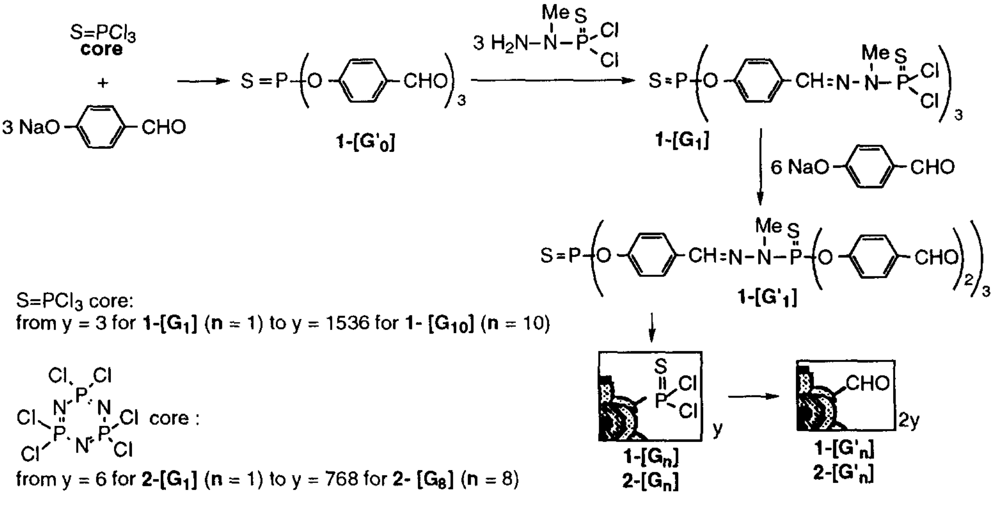
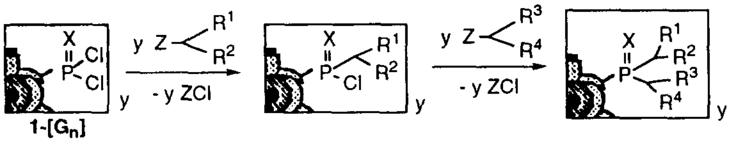
Abstract: A specific monosubstitution on each $P(X)(NH\text{-}CH_2\text{-}CH{=}CH_2)_2$ terminal group (X = O, S) of phosphorus dendrimers is described, from generation 1 to generation 7. This reaction allows to isolate compounds which possess simultaneously up to 192 phosphine, 192 N-H and 384 allyl groups. Preliminary experiments show that these functionalized dendrimers are able to complex transition metals such as iron and tungsten. Copyright © 1996 Elsevier Science Ltd

The synthesis of functionalized macromolecules of defined structure, namely dendrimers, has induced much work in the past few years, both in organic and heteroatomic chemistry.[1] The most striking feature of dendrimers is the presence of dozens or hundreds of functions which are easily accessible, as they are located at the periphery; thus attention is now focussed on the reactivity of the surface.

We have recently reported several methods of synthesis of phosphorus dendrimers.[2] The best one is a two step method which gives alternatively on the surface CHO or $P(S)Cl_2$ functions, depending on the step considered and illustrated below starting from the the trifunctional core $(S)PCl_3$[2a] or the hexafuntional core $N_3P_3Cl_6$.[2d]

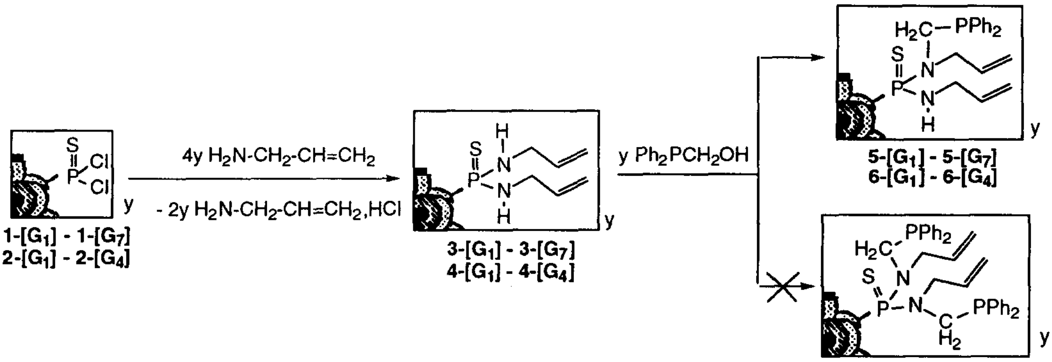


The end groups display a versatile reactivity,[3] including for the first time the synthesis of multi tri- and tetra-functionalized dendrimers.[3d] These compounds bear simultaneously many groups of three or four different functions on the surface. Their obtainment is mainly due to a specific monosubstitution on each $P(X)Cl_2$ terminal function (X = O, S; y = number of terminal groups; Z = H, Na...).



We now report a new specific monosubstitution which does not occur on phosphorus but on the substituents linked to phosphorus. The first step of this synthesis consists in grafting allylamine on **1-[Gn]** or **2-[Gn]**. This quantitative reaction allows to isolate fully substituted dendrimers which possess $P(S)[NH-CH_2-CH=CH_2]_2$ end groups, from generation 1 to 7 for the trifunctional core (**3-[G_1] - 3[G_7]**),[3c] and from generation 1 to 4 for the hexafunctional core (**4-[G_1] - 4[G_4]**).

The second step is a Mannich type reaction using Ph_2P-CH_2-OH, generated from neat Ph_2P-H and paraformaldehyde heated together for 90 min at 120°C. A solution of Ph_2P-CH_2-OH and dendrimer **3-[G_1] - 3[G_7]** or **4-[G_1] - 4[G_4]** in THF is heated for 3 days at 80°C. The reaction is monitored by ^{31}P NMR which shows the disappearance of the singlet corresponding to the $P(S)[NH-CH_2-CH=CH_2]_2$ end groups (δ = 68.7 ppm) on behalf of two doublets at δ = 72.4 ppm ($^3J_{PP}$ = 5 Hz) and δ = - 21.0 ppm ($^3J_{PP}$ = 5 Hz) corresponding to P=S and PPh_2, respectively. The presence of these doublets gives evidence of the reaction of only one N-H group of each $P(S)[NH-CH_2-CH=CH_2]_2$ end groups. Indeed, the reaction of both N-H group would lead to a triplet in ^{31}P NMR for the P=S groups. We have never observed this type of signal, even when an excess of Ph_2P-CH_2-OH and a higher temperature are used. The specific formation of compounds **5-[G_1] - 5[G_7]** and **6-[G_1] - 6[G_4]** is confirmed by ^1H NMR, with the presence of remaining N-H groups (δ = 3.3 ppm, br. s) and by ^{13}C NMR which shows the presence of two types of $N-CH_2-CH=CH_2$ groups at δ = 43.6 and 50.0 ppm (s, $N-CH_2$), δ = 115.4 and 118.2 ppm (s, $=CH_2$) and δ = 134.4 (s, CH) and 136.2 ppm (d, $^3J_{CP=S}$ = 8 Hz, CH).[4]



Thus, these dendrimers bear up to 48 PPh_2, 48 N-H and 96 allyl groups for the series built from the N_3P_3 core, **6-[G_n]**, and up to 192 PPh_2, 192 N-H and 384 allyl groups for the series built from the P=S core, **5-[G_n]** (see Table below).

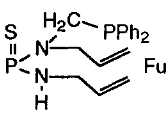
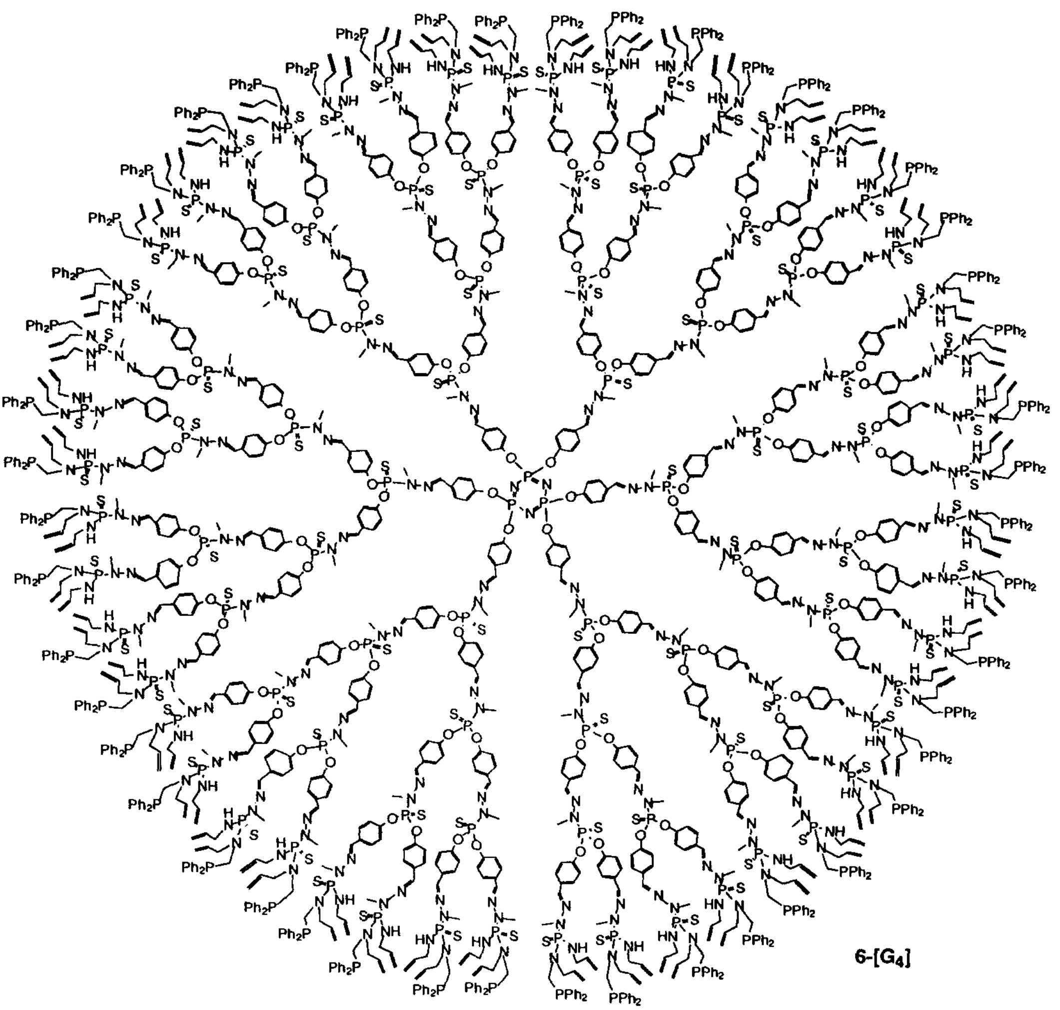

$S=P(NH-CH_2-CH=CH_2)(N(CH_2PPh_2)-CH_2-CH=CH_2)$

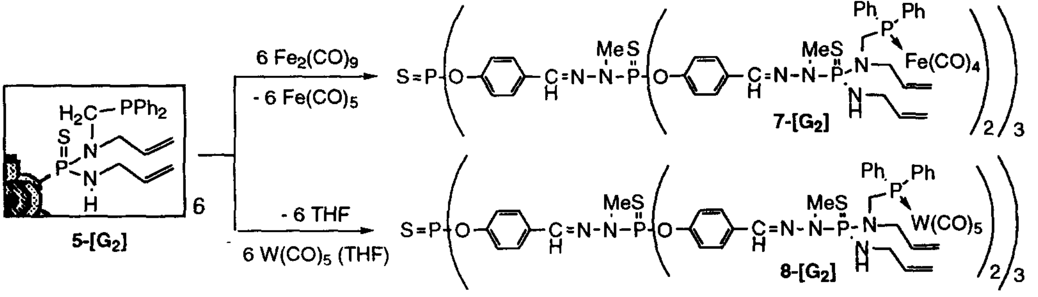
Table. Number of Terminal $P(S)[N(CH_2PPh_2)CH_2CH=CH_2][NH-CH_2CH=CH_2]$ Functions (y) for Dendrimers **5-[G_1] - 5-[G_7], 6-[G_1] - 6-[G_4]**

Generation n	1	2	3	4	5	6	7
S=P core Compound	**5-[G_1]**	**5-[G_2]**	**5-[G_3]**	**5-[G_4]**	**5-[G_5]**	**5-[G_6]**	**5-[G_7]**
Functions	3	6	12	24	48	96	192
N_3P_3 core Compound	**6-[G_1]**	**6-[G_2]**	**6-[G_3]**	**6-[G_4]**			
Functions	6	12	24	48			



6-[G₄]

Preliminary complexation experiments of the phosphine groups of dendrimer **5-[G$_2$]** indicate a classical behaviour toward $Fe_2(CO)_9$ and $W(CO)_5(THF)$ to give dendrimers **7-[G$_2$]** and **8-[G$_2$]**, with 6 $Fe(CO)_4$ or 6 $W(CO)_5$ groups, respectively. The main characteristic of these compounds is the deshielding of the PPh_2 signal in ^{31}P NMR: $\delta = 68.5$ (d, $^3J_{PP_2} = 13.6$ Hz) for **7-[G$_2$]** and $\delta = 16.0$ (d, $^3J_{PP_2} = 7.0$ Hz, $^1J_{PW} = 232.6$ Hz) for **8-[G$_2$]**, to be compared with $\delta = -21.1$ (d, $^3J_{PP_2} = 5.1$ Hz) for **5-[G$_2$]**. No evidence for the involvement of the allyl groups in the complexation can be found.



5-[G$_2$] **7-[G$_2$]** **8-[G$_2$]**

References and notes

1. For reviews on dendrimers see for example: (a) Tomalia, D. A.; Naylor, A. M.; Goddart III, W. A. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138.(b) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413. (c) Moorefield, C. N.; Newkome, G. R. in *Advances in Dendritic Molecules*, Vol. 1; Newkome, G. R. Ed; JAI Press: Greenwich CT, USA 1994; pp. 1. (d) Caminade, A.-M.; Majoral, J.-P. *Main Group Chemistry News* **1995**, *1*, 14. (e) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 876.
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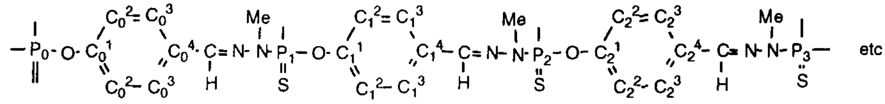
4. Selected spectroscopic data. The numbering of the dendrimer skeleton used for ^{13}C and ^{31}P NMR is depicted on the following scheme:



5-[G$_7$]: white powder; 93% yield. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): - 20.9 (d, $^3J_{PP7}$ = 4.3 Hz, PPh_2), 62.3 (br s, P_1, P_2, P_3, P_4, P_5, P_6), 72.1 (d, $^3J_{P7P}$ = 4.3 Hz, P_7) ppm; ^1H NMR (δ, $CDCl_3$): 3.1 (m, 1143 H, N-CH_3), 3.3 (br s, 192 H, N-H), 3.5-4.1 (m, 768 H, N-$C\underline{H}_2$-CH=CH_2), 4.1 (d, $^2J_{HP}$ = 11.4 Hz, 384 H, CH_2P), 5.0-5.2 (m, 768 H, N-CH_2-CH=$C\underline{H}_2$), 5.8-6.0 (m, 384 H, N-CH_2-C$\underline{H}$=CH_2), 7.1-7.7 (m, 5745 H, C_6H_5, C_6H_4, CH=N) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 31.6 (d, $^2J_{CP7}$ = 11.5 Hz, P_7NMe), 33.1 (br d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$ = 12.8 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}$NMe), 43.6 (s, HN-$\underline{C}H_2$-CH=$CH_2$), 48.4 (d, $^1J_{CP}$ = 9.1 Hz, CH_2-P), 50.0 (s, CH_2N-$\underline{C}H_2$-CH=CH_2), 115.4 (s, HN-CH_2-CH=$\underline{C}H_2$), 118.2 (s, CH_2N-CH_2-CH=$\underline{C}H_2$), 121.7 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}^2$), 127.6 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6}^3$), 128.5 (d, $^3J_{CP}$ = 6.1 Hz, *m*-C_6H_5), 128.7 (d, $^4J_{CP}$ = 9.0 Hz, *p*-C_6H_5), 132.8 (s, C_6^4), 133.0 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5}^4$), 133.4 (d, $^2J_{CP}$ = 18.0 Hz, *o*-C_6H_5), 134.4 (s, CH_2N-CH_2-$\underline{C}$H=CH_2), 135.4 (d, $^3J_{CP7}$ = 11.8 Hz, $(CH=N)_6$), 136.2 (d, $^3J_{CP7}$ = 8.3 Hz, HN-CH_2-$\underline{C}$H=CH_2), 137.0 (d, $^1J_{CP}$ = 14.1 Hz, *i*-C_6H_5), 138.9 (m, $(CH=N)_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5}$), 150.7 (d, $^2J_{CP6}$ = 7.8 Hz, C_6^1), 151.4 (m, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5}^1$) ppm; IR (KBr): 3369 ($\nu_{NH}$) cm^{-1}.

6-[G$_4$]: white powder; 94% yield. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): - 21.2 (d, $^3J_{PP4}$ = 4.5 Hz, PPh_2), 8.0 (s, P_0), 62.0 (br s, P_1, P_2, P_3), 72.3 (d, $^3J_{P4P}$ = 4.5 Hz, P_4) ppm; ^1H NMR (δ, $CDCl_3$): 3.1 (d, $^3J_{PP1\text{-}2\text{-}3\text{-}4}$ = 9.2 Hz, 270 H, N-CH_3), 3.2 (br s, 48 H, N-H), 3.6-3.9 (m, 192 H, N-$C\underline{H}_2$-CH=CH_2), 4.0 (d, $^2J_{HP}$ = 10.7 Hz, 96 H, CH_2P), 4.9-5.1 (m, 192 H, N-CH_2-CH=$C\underline{H}_2$), 5.6-5.8 (m, 96 H, N-CH_2-C$\underline{H}$=CH_2), 7.1-7.7 (m, 930 H, C_6H_5, C_6H_4, CH=N) ppm; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 31.5 (d, $^2J_{CP4}$ = 12.3 Hz, P_4NMe), 33.0 (br d, $^2J_{CP1\text{-}2\text{-}3}$ = 11.5 Hz, $P_{1\text{-}2\text{-}3}$NMe), 43.6 (s, HN-$\underline{C}H_2$-CH=CH_2), 48.2 (d, $^1J_{CP}$ = 10.3 Hz, CH_2-P), 49.8 (s, CH_2N-$\underline{C}H_2$-CH=CH_2), 115.3 (s, HN-CH_2-CH=$\underline{C}H_2$), 118.1 (s, CH_2N-CH_2-CH=$\underline{C}H_2$), 121.5 (br s, $C_{0\text{-}1\text{-}2\text{-}3}^2$), 127.4 (s, $C_{0\text{-}1\text{-}2\text{-}3}^3$), 128.3 (d, $^3J_{CP}$ = 6.1 Hz, *m*-C_6H_5), 128.7 (d, $^4J_{CP}$ = 9.9 Hz, *p*-C_6H_5), 132.2 (s, $C_{0\text{-}1\text{-}2}^4$), 132.8 (s, C_3^4), 133.3 (d, $^2J_{CP}$ = 20.4 Hz, *o*-C_6H_5), 134.2 (s, CH_2N-CH_2-$\underline{C}$H=CH_2), 135.3 (d, $^3J_{CP4}$ = 11.9 Hz, $(CH=N)_4$), 136.1 (d, $^3J_{CP4}$ = 8.4 Hz, HN-CH_2-$\underline{C}$H=CH_2), 136.8 (d, $^1J_{CP}$ = 13.9 Hz, *i*-C_6H_5), 138.9 (m, $(CH=N)_{0\text{-}1\text{-}2}$), 150.5 (d, $^2J_{CP3}$ = 7.0 Hz, C_3^1), 151.2 (m, $C_{0\text{-}1\text{-}2}^1$) ppm; IR (KBr): 3369 ($\nu_{NH}$) cm^{-1}.

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