Synthesis and Core and Surface Reactivity of Phosphorus-Based Dendrons

Rosa-María Sebastián,[a] Laurent Griffe,[a] Cédric-Olivier Turrin,[a] Bruno Donnadieu,[a] Anne-Marie Caminade,*[a] and Jean-Pierre Majoral*[a]

Keywords: Azides / Dendrimers / Dendrons / N,P ligands / Phosphorus

A series of phosphorus-containing dendrons is synthesized starting from a unique precursor $(EtO)_2P(O)CH{=}CHC_6H_4PPh_2$ (**3-G$_0$**), whose X-ray crystal structure shows an extended planarity between both phosphorus. Staudinger reactions with functionalized azides on the phosphino group are the first step for the growth of the dendrons, which is continued using a divergent method. Several types of reactions are performed on dendrons of several sizes, either at the level of the core or of the surface. The specific addition of methyl triflate to P=S and trimethylsilyl triflate to P=O at the level of the core affords a dicationic species. A ^{13}C NMR spectroscopic study indicates to what extent the charges are delocalized. Phosphanes are grafted on the surface of a second-generation dendron, and used for the complexation of $PdCl_2$. Both compounds possess five different types of phosphorus atoms, which helps in characterizing them by ^{31}P NMR spectroscopy.

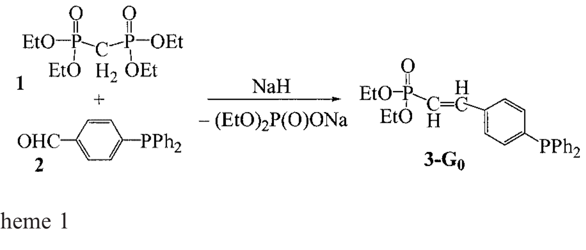
Introduction

Dendrons[1] are dendritic wedges that differ from classical dendrimers[2] by the presence of a functional group at the level of the core. Such compounds can be built using either a convergent[3] or a divergent[4] process, and they have found applications as building blocks for the rapid synthesis of dendrimers[5] or for the coating of the surface of various materials, for example.[6] The nature of the function located at the core is of crucial importance when synthesizing dendrons, particularly if a divergent process is used. Indeed, this function is present from the beginning of the synthesis and hence it must be compatible with the whole synthetic process while remaining available for further reactions after the growth of the dendron. Due to the wide range of uses and applications of phosphonates in organic synthesis, biology and materials chemistry,[7] we decided to graft a phosphonate at the core, linked through a potentially conjugated linkage, which may act as a probe for sensing further reactivity.

We have already reported the divergent synthesis of phosphorus-containing dendrons[4,8,9] and dendrimers,[10] and shown that ^{31}P NMR spectroscopy is an extraordinarily useful tool for characterizing such compounds. However, when the chemical structure is similar at each layer, a partial overlap of signals may occur.[11] We and others have shown that using two[12] or three[13,14] types of chemical environment around the phosphorus atoms allows an easier characterization. We report in this paper the synthesis and characterization of a series of dendrons having a phosphonate at the core and up to five different types of phosphorus atoms in the structure; these are clearly distinguishable by ^{31}P NMR spectroscopy. Furthermore, these compounds possess a versatile reactivity at every step of the synthesis, as will be illustrated by three very different examples.

Results and Discussion

The method used for grafting the phosphonate at the core consists of the Horner−Wadsworth−Emmons reaction[15] of tetraethylmethylene *gem*-diphosphonate **1** with diphenylphosphino benzaldehyde **2** in the presence of NaH that we have already applied to the surface of dendrimers[16] (Scheme 1). The reaction creates a C=C bond connecting the phosphonate to the aryl group. The resulting vinyl phosphonate derivative **3-G$_0$** was isolated in quantitative yield. The expected *E*-configuration of the alkene bond is shown in the ^{1}H NMR spectrum by the large value of the $^3J_{H,H}$ coupling constant (17.2 Hz). Single crystals of **3-G$_0$** were obtained by slow evaporation of a solution in CH_2Cl_2 and allowed the determination of its structure by X-ray diffrac-



Scheme 1

---

[a] Laboratoire de Chimie de Coordination CNRS
205, Route de Narbonne, 31077 Toulouse Cedex 4, France
Fax: +33-(0)5-61553003
E-mail: caminade@lcc-toulouse.fr
majoral@lcc-toulouse.fr

DOI: 10.1002/ejic.200400016

tion. The ORTEP drawing is shown in Figure 1 and confirms the *E*-configuration of the C=C bond. All atoms from P2 to O3 are in a plane (Rms deviation 0.0685), indicating an extended conjugation of 11 atoms.

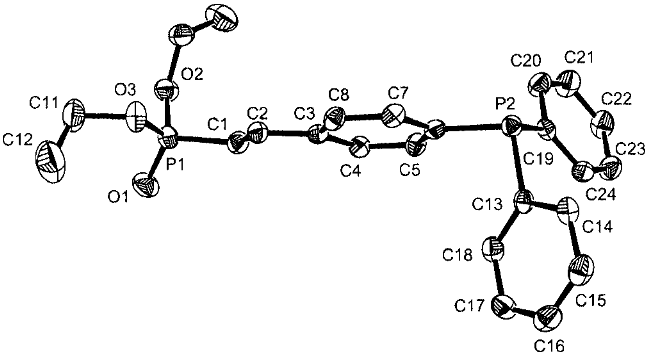
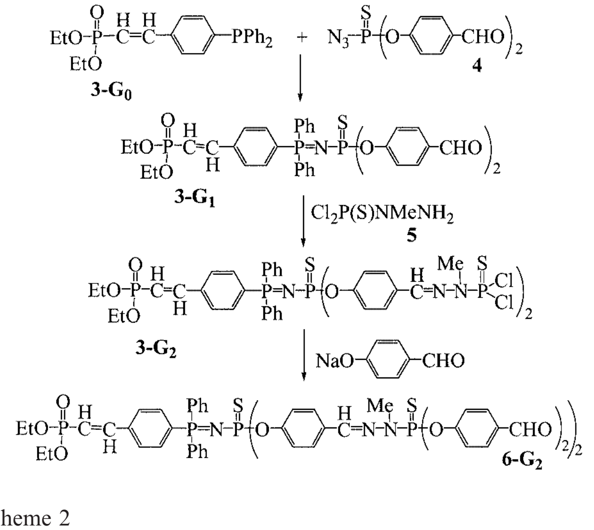


Figure 1. ORTEP drawing of **3-G$_0$**; selected bond lengths (Å) and angles (°): P1−O1 1.4605(16), P1−O2 1.5754(15), P1−O3 1.5794(16), P1−C1 1.775(2), C1−C2 1.322(3), P2−C6 1.8328(19), P2−C13 1.839(2), P2−C19 1.8421(19); P1−C1−C2 125.04(17), C1−C2−C3 126.25(19)

Compound **3-G$_0$** is the starting material for the synthesis of various dendrons. Indeed, the presence of a phosphane allows it to undergo Staudinger reactions with functionalized azides such as compound **4**, which affords the first generation dendron **3-G$_1$** (Scheme 2). As expected,[17] the P=N−P=S linkage created by the reaction is characterized in the ^{31}P NMR spectrum by two doublets at δ = 14.4 (P=N) and 50.2 (P=S) ppm with $^2J_{P,P}$ = 31 Hz. In the ^{13}C NMR spectrum a dramatic shielding of the signals corresponding to the carbons linked to the phosphorus that undergoes the reaction is observed ($\Delta\delta$ = −9.31 ppm for $C_{ipso}PPh_2$; $\Delta\delta$ = −10.65 ppm for $C_{ipso}PC_6H_4$) together with a very important increase of the $^1J_{C,P}$ coupling constant. More interestingly, the Staudinger reaction also induces changes for the vinyl linkage, where the signal corresponding to the =CH linked to C_6H_4 is shielded, whereas the signal corresponding to (O)P-CH= is deshielded ($\Delta\delta$ = +3.44 ppm), confirming a conjugation through the aromatic and vinyl linkages (Figure 2).



Scheme 2

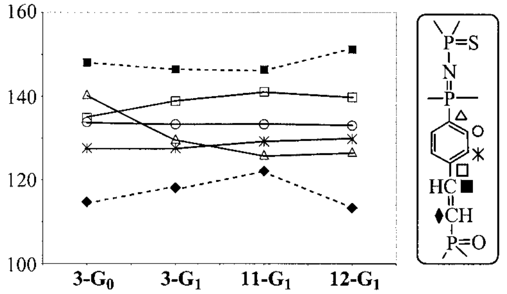
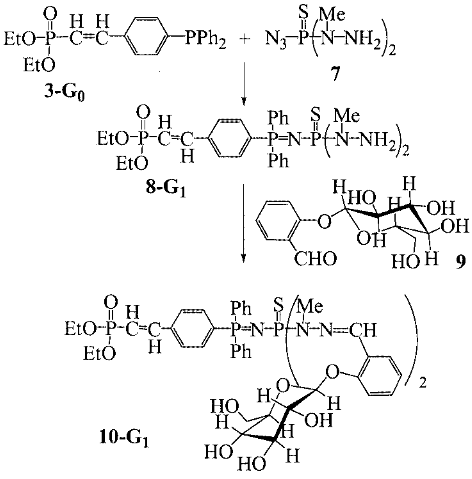


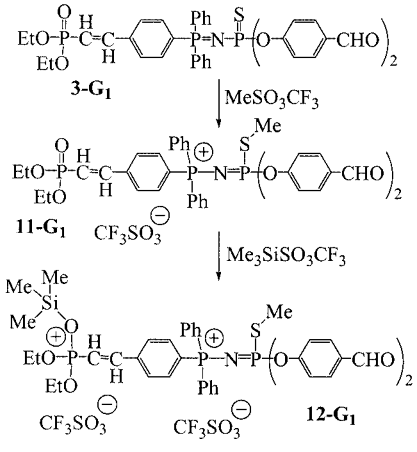
Figure 2. Variation of the chemical shifts (^{13}C NMR) for all carbon atoms located from P(O) to P for four compounds (**3-G$_0$**, **3-G$_1$**, **11-G$_1$**, and **12-G$_1$**)

To continue the growth of the dendron, our classical method of synthesis of dendrimers[18,19] was applied starting from the aldehydes of **3-G$_1$**, and using the phosphorhydrazide **5** to generate dendron **3-G$_2$**. Then, the nucleophilic substitution of Cl with hydroxybenzaldehyde sodium salt afforded compound **6-G$_2$**. It is noteworthy that none of these reactions has an influence on the vinylphosphonate group located at the core, as shown by ^{31}P NMR spectroscopy, with the presence of the singlet of the P=O group (δ = 18.2 ppm) together with the singlet of the P=S end groups (δ = 60.7 ppm) and both doublets corresponding to the P=N−P=S linkage (δ = 13.7 and 51.8 ppm, respectively).

Thus, the growth of the dendron could have been pursued to higher generations, as we have already shown with dendrons containing other types of functions at the core,[4,8,9,20] but we prefer to show the versatility and adaptability of this method of synthesis at every step, including starting from **3-G$_0$**. Indeed, other types of functionalized azides can be used, as shown by the reaction with compound **7** affording **8-G$_1$** (Scheme 3). Here also, the Staudinger reaction induces the appearance of two doublets in the ^{31}P NMR spectrum at δ = 12.8 (P=N) and 71.2 (P=S) ppm with $^2J_{P,P}$ = 17.2 Hz. Obviously, the presence of NH_2 groups opens the way to a tremendous number of reactions, in particular condensations with functionalized aldehydes. As an illustration, the carbohydrate derivative **9** (helicin) was condensed with **8-G$_1$**. The condensation induces an important shielding in the ^{31}P NMR spectrum for the signal corresponding to the P=S group, from δ = 71.2 ppm for **8-G$_1$** to δ = 62.5 ppm for **10-G$_1$**. A careful examination of the ^{1}H and ^{13}C NMR spectra of **10-G$_1$** shows that several signals corresponding to the helicin and hydrazone moieties are split into two series of signals in a 1:1 ratio; for example, the NCH_3 groups give two doublets at δ = 33.89 and 34.04 ppm. Such splitting might be ascribed to *E* and *Z* isomers of the hydrazone bond (C=N) with one *E* and one *Z* bond for each molecule of **10-G$_1$**. Phosphorhydrazone bonds are generally in the *E* configuration, thus the formation of a *Z* isomer might be due to the occurrence of hydrogen bonds, which forces one hydrazone linkage to be in the *Z* form, as previously noticed on the surface of dendrimers.[21] Due to the carbohydrate moieties, **10-G$_1$** is soluble in water, whereas all the other dendrons described in this paper are not.



Scheme 3

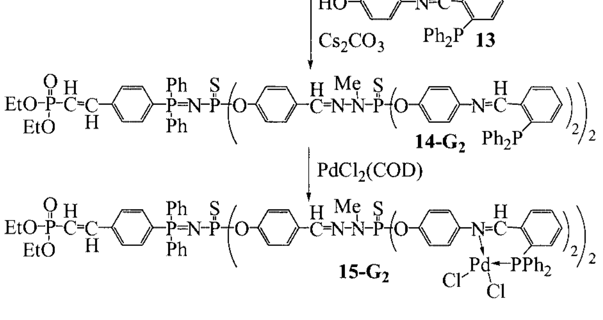


Scheme 4

We also tested another type of reactivity with compound **3-G$_1$** — alkylation reactions — with the aim of detecting to what extent the positive charge could be delocalized.[22] One equivalent of the strong alkylating reagent methyl trifluoromethanesulfonate was added to **3-G$_1$** (Scheme 4). We have already shown that this reagent is able to alkylate the sulfur atom included in a P=N−P=S linkage,[13,17,23] but such a reaction has never been performed in the presence of a phosphonate group, although we have reported the specific alkylation of P=S in macrocycles bearing phosphane oxide groups.[24] The ^{31}P NMR spectrum of the resulting compound **11-G$_1$** shows without any ambiguity that the alkylation occurs exclusively at the P=S group. Indeed, a $\Delta\delta$ value of −27 ppm was measured for the signal corresponding to P=S, whereas it is only −1 ppm for the P=O group, on going from **3-G$_1$** to **11-G$_1$**. Both signals corresponding to P=N (δ = 22.2 ppm) and P=S (δ = 23.1 ppm) are close; the assignment of the chemical shift was made by proton-coupled ^{31}P NMR spectroscopy, which gives a coupling constant of 18.2 Hz for the signal at δ = 23.1 ppm (P−S−Me). The positive charge is delocalized to some extent onto the adjacent P=N group ($\Delta\delta$ = +8 ppm). In view of the extended planarity seen in the X-ray structure of **3-G$_0$**, and the modification of the ^{13}C NMR spectra on going from **3-G$_0$** to **3-G$_1$**, the charge might even be delocalized all the way along the chain up to the phosphonate group. The ^{13}C NMR spectrum shows a deshielding of the signal corresponding to (O)P-*C*H=, which should correspond to a partial positive charge on this atom (Figure 2, rhombuses). However, the absence of a variation of the chemical shift corresponding to P=O seems to preclude an extension of the delocalization up to it, and is in agreement with the structure of **3-G$_0$** obtained by X-ray diffraction in which the oxygen of P=O lies outside the main plane.

This assumption was reinforced by checking the reactivity of trimethylsilyl trifluoromethanesulfonate with **11-G$_1$**, since we have already shown that it is able to react with phosphane oxides.[25] Indeed, the presence of a positive charge on P=O should hamper further addition of cations to this group. The reaction monitored by ^{31}P NMR spectroscopy shows a deshielding of the signal corresponding to the P=O group ($\Delta\delta$ = 4 ppm) whereas no change is observed for the other signals. The dicationic species **12-G$_1$** was obtained quantitatively. The ^{13}C NMR spectrum of **12-G$_1$** shows only modifications for the vinyl group, with a shielding of the carbon linked to phosphorus ($\Delta\delta$ = −9 ppm) and a deshielding of the other carbon ($\Delta\delta$ = 5 ppm) (Figure 2). Thus, the delocalization of the second positive charge only has an influence on the (O)P−CH=CH linkage.

The last example illustrating the versatile reactivity of this series of dendrons concerns **3-G$_2$**. Its P(S)Cl$_2$ end-groups can be reacted with various functionalized phenols such as **13**, which affords dendron **14-G$_2$** (Scheme 5). These phosphanyl end-groups are used because they are potential N,P ligands. Indeed, we have shown previously that the corresponding Pd complexes linked to the surface of dendrimers efficiently catalyze Stille coupling reactions.[26] The palladium complex **15-G$_2$** is readily obtained by reaction with [PdCl$_2$(COD)]. Here again the ^{31}P NMR spectrum gives very informative data for the characterization. Fig-



Scheme 5

ure 3 shows the spectrum of **15-G$_2$**, with five different types of phosphorus atoms clearly distinguishable, and in the expected ratio.

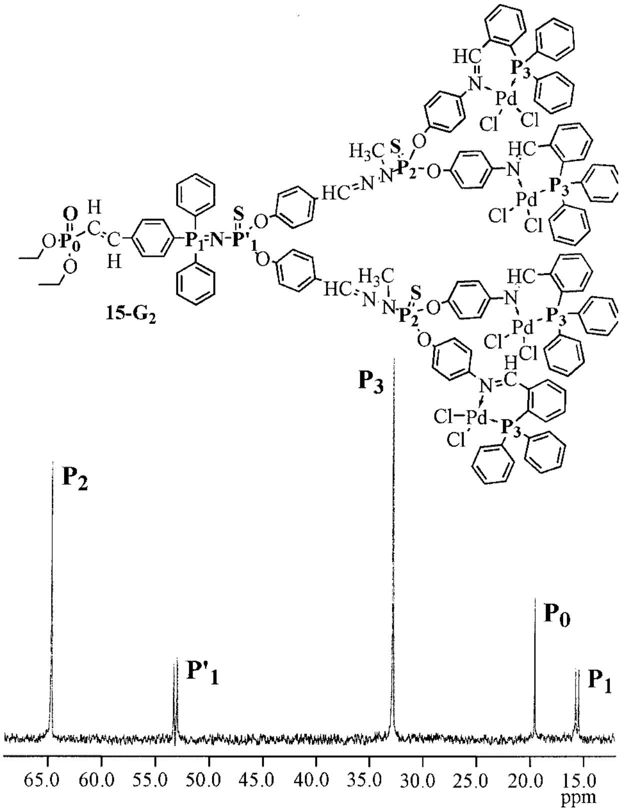


Figure 3. ^{31}P NMR spectrum and chemical structure of **15-G$_2$**

Conclusion

We have shown in this paper that compound **3-G$_0$** is a multifunctional diphosphorus derivative, readily usable as the core of various dendrons. These dendrons contain up to five different types of phosphorus groups, which act as sensitive labels that are able to detect subtle and remote chemical modification, as shown by ^{31}P NMR spectroscopy. These dendrons also possess a versatile reactivity both at the level of the core and of the end groups that is adaptable depending on the type of use desired. As an illustration, we have given three very different examples concerning modification of the solubility, alkylation with delocalization of the charges, and grafting of N,P ligands as end-groups, along with a preliminary study of their complexation properties. Obviously, many other examples of reactions can be envisaged, in particular concerning the use of phosphonates for the grafting of dendrons on the surface of various materials. Indeed, it is known that phosphonates are able to react, for instance, with alumina[27] and titania particles.[28] Thus, compound **15-G$_2$** could be used as precursor of heterogeneous catalysts.

Experimental Section

General Remarks: All manipulations were carried out with standard high vacuum and dry-argon techniques. The solvents were freshly dried and distilled (THF and diethyl ether over sodium/benzophenone; pentane and CH_2Cl_2 over phosphorus pentoxide; toluene over sodium); they were degassed prior to use in the case of experiments using trivalent phosphorus derivatives. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, DPX 300 or AMX 400 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR and $SiMe_4$ for ^{1}H and ^{13}C NMR spectroscopy. The attribution of the ^{13}C NMR signals was performed by using J_{mod}, two dimensional HMBC, and HMQC, Broad Band or CW ^{31}P decoupling experiments when necessary. The numbering used for the NMR assignments is depicted in Figure 4. Compounds **2**,[29] **4**,[30] **7**,[30] and **13**[26] were synthesized as reported previously.

Phosphane 3-G$_0$: A solution of $(EtO)_2P(O)CH_2P(O)(OEt)_2$ (0.500 g, 1.680 mmol) in THF (5 mL) was added to a suspension of NaH (0.043 g, 1.680 mmol) in THF (15 mL). After stirring for 10 min a clear solution was obtained. A solution of $CHOC_6H_4PPh_2$ (0.490 g, 1.68 mmol) in THF (5 mL) was then added dropwise. The resulting mixture was stirred overnight, then H_2O (10 mL) was added. The resulting mixture was concentrated under vacuum to eliminate THF, then CH_2Cl_2 (10 mL) was added. The organic phase was recovered, and the water phase was washed twice with CH_2Cl_2. The organic layers were combined and the solvents evaporated to dryness to afford a pale yellow powder. **3-G$_0$** was purified by column chromatography on silica gel (eluent: ethyl acetate) to afford a white powder in 99% yield (0.700 g). Translucent crystals suitable for X-ray diffraction were obtained after a slow evaporation of a solution in CH_2Cl_2. ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (t, $^{3}J_{H,H} = 7.1$ Hz, 6 H, CH_3), 4.09 (dt, $^{3}J_{H,H} = 7.1$, $^{3}J_{H,P} = 14.3$ Hz, 4 H, CH_2), 6.25 (t, $^{3}J_{H,H} = {}^{2}J_{H,P} = 17.5$ Hz, 1 H, $=CH-P_0$), 7.21−7.46 (m, 14 H, H_{Arom}), 7.51 (d, $^{3}J_{H,H} = 17.5$ Hz, 1 H, $CH=CH-P_0$) ppm. $^{13}C\{^{1}H\}$

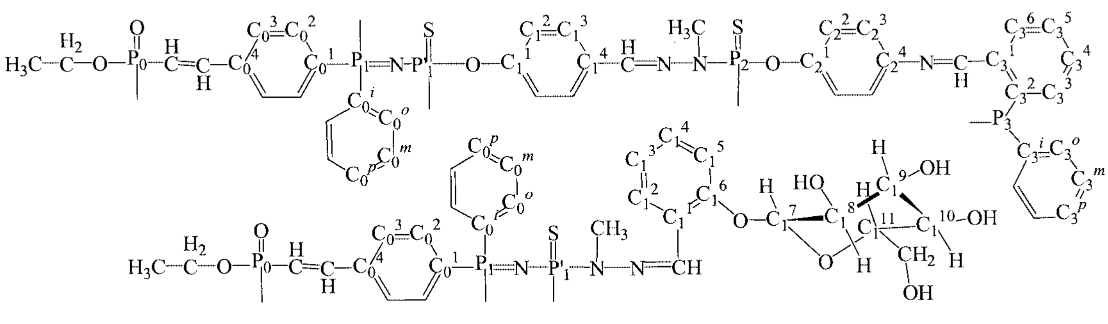


Figure 4. Numbering used for NMR spectroscopy

NMR ($CDCl_3$): $\delta = 16.42$ (d, $^3J_{C,P} = 6.0$ Hz, CH_3), 61.84 (d, $^2J_{C,P} = 5.7$ Hz, CH_2), 114.68 (d, $^1J_{C,P} = 191.2$ Hz, =CH-P_0), 127.60 (d, $^3J_{C,P} = 7.3$ Hz, C_0^3), 128.62 (d, $^3J_{C,P} = 6.0$ Hz, C_0^m), 128.98 (s, C_0^p), 133.79 (d, $^2J_{C,P} = 21.2$ Hz, C_0^o), 133.83 (d, $^2J_{C,P} = 16.3$ Hz, C_0^2), 134.93 (d, $^3J_{C,P} = 23.4$ Hz, C_0^4), 136.50 (d, $^1J_{C,P} = 10.1$ Hz, C_0^i), 140.50 (d, $^1J_{C,P} = 13.5$ Hz, C_0^1), 148.07 (d, $^1J_{C,P} = 7.6$ Hz, *C*H=CH-P_0) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -5.2$ (s, P_1), 19.5 (s, P_0) ppm. $C_{24}H_{26}O_3P_2$ (424.41): calcd. C 67.92, H 6.17; found C 67.96, H 6.19.

Dendron 3-G_1: CH_2Cl_2 (10 mL) was added to a powdered mixture of **3-G_0** (0.302 g, 0.712 mmol) and the azide $N_3P(S)(OC_6H_4CHO)_2$ (0.247 g, 0.712 mmol). A rapid evolution of nitrogen was observed. The solution was stirred overnight then evaporated to dryness to afford **3-G_1** as a pale yellow powder in 98% yield (0.520 g). A strict 1:1 ratio must be respected between **3-G_0** and the azide, because numerous washings of **3-G_1** did not allow the elimination of the unreacted starting materials. ^1H NMR ($CDCl_3$): $\delta = 1.30$ (t, $^3J_{H,H} = 7.1$ Hz, 6 H, CH_3), 4.09 (dt, $^3J_{H,H} = 7.1$, $^3J_{H,P} = 14.6$ Hz, 4 H, CH_2), 6.35 (t, $^3J_{H,H} = {^2J_{H,P}} = 17.2$ Hz, 1 H, =CH-P_0), 7.26 (d, $^3J_{H,H} = 8.0$ Hz, 4 H, H-C_1^2), 7.37−7.66 (m, 14 H, H_{Arom}), 7.55 (d, $^3J_{H,H} = 17.2$ Hz, 1 H, C*H*=CH-P_0), 7.73 (d, $^3J_{H,H} = 8.0$ Hz, 4 H, H-C_1^3), 9.86 (s, 2 H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 16.39$ (d, $^3J_{C,P} = 5.9$ Hz, CH_3), 62.07 (d, $^2J_{C,P} = 5.9$ Hz, CH_2), 118.12 (d, $^1J_{C,P} = 189.6$ Hz, =CH-P_0), 122.03 (d, $^3J_{C,P} = 4.1$ Hz, C_1^2), 127.19 (dd, $^1J_{C,P} = 106.0$, $^3J_{C,P} = 3.8$ Hz, C_0^i), 127.63 (d, $^3J_{C,P} = 13.5$ Hz, C_0^3), 128.84 (d, $^3J_{C,P} = 13.7$ Hz, C_0^m), 129.85 (dd, $^1J_{C,P} = 113.0$, $^3J_{C,P} = 3.5$ Hz, C_0^1), 131.16 (s, C_1^3), 132.60 (s, C_1^4), 132.64 (d, $^2J_{C,P} = 11.7$ Hz, C_0^o), 133.01 (s, C_0^p), 133.27 (d, $^2J_{C,P} = 11.6$ Hz, C_0^2), 138.95 (d, $^3J_{C,P} = 24.3$ Hz, C_0^4), 146.49 (d, $^2J_{C,P} = 6.6$ Hz, *C*H=CH-P_0), 156.79 (d, $^2J_{C,P} = 9.4$ Hz, C_1^1), 190.96 (s, CHO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.4$ (d, $^2J_{P,P} = 31.0$ Hz, P_1), 18.0 (s, P_0), 50.2 (d, $^2J_{P,P} = 31.0$ Hz, P'_1) ppm. $C_{38}H_{36}NO_7P_3S$ (743.69): calcd. C 61.37, H 4.88, N 1.88; found C 61.56, H 4.91, N 1.79.

Dendron 3-G_2: A solution of $H_2NNMeP(S)Cl_2$ in $CHCl_3$ (1.12 mL, 0.260 mmol) was added to a solution of **3-G_1** (0.088 g, 0.118 mmol) in THF (10 mL). The resulting solution was stirred for 4 hours then evaporated to dryness to afford an oil. This oil was washed three times with CH_2Cl_2/pentane then evaporated to dryness to afford **3-G_2** as a pale yellow powder in 81% yield (0.102 g). ^1H NMR ($CDCl_3$): $\delta = 1.34$ (t, $^3J_{H,H} = 6.9$ Hz, 6 H, CH_2-CH_3), 3.46 (d, $^3J_{H,P} = 7.0$ Hz, 6 H, N-CH_3), 4.13 (dt, $^3J_{H,H} = 6.9$, $^3J_{H,P} = 14.2$ Hz, 4 H, CH_2), 6.35 (t, $^3J_{H,H} = {^2J_{H,P}} = 17.2$ Hz, 1 H, =CH-P_0), 7.21 (d, $^3J_{H,H} = 7.8$ Hz, 4 H, H-C_1^2), 7.58 (d, $^3J_{H,H} = 7.8$ Hz, 4 H, H-C_1^3), 7.44−7.65 (m, 17 H, H_{Arom}, CH=N, CH=CH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 16.26$ (d, $^3J_{C,P} = 6.4$ Hz, CH_2-CH_3), 31.68 (d, $^2J_{C,P} = 13.9$ Hz, N-CH_3), 62.09 (d, $^2J_{C,P} = 5.8$ Hz, CH_2), 117.28 (d, $^1J_{C,P} = 190.7$ Hz, =CH-P_0), 121.89 (d, $^3J_{C,P} = 5.0$ Hz, C_1^2), 127.49 (d, $^3J_{C,P} = 13.6$ Hz, C_0^3), 128.00 (dd, $^1J_{C,P} = 107.0$, $^3J_{C,P} = 4.0$ Hz, C_0^i), 128.24 (s, C_1^3), 128.61 (d, $^3J_{C,P} = 13.1$ Hz, C_0^m), 130.09 (s, C_1^4), 130.15 (dd, $^1J_{C,P} = 110.0$, $^3J_{C,P} = 4.0$ Hz, C_0^1), 132.56 (d, $^2J_{C,P} = 10.4$ Hz, C_0^o), 132.67 (s, C_0^p), 133.18 (d, $^2J_{C,P} = 11.4$ Hz, C_0^2), 138.44 (dd, $^3J_{C,P} = 23.3$, $^4J_{C,P} = 2.9$ Hz, C_0^4), 141.08 (d, $^3J_{C,P} = 18.7$ Hz, CH=N-N), 146.76 (d, $^2J_{C,P} = 5.5$ Hz, *C*H=CH-P_0), 153.35 (d, $^2J_{C,P} = 14.8$ Hz, C_1^1) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 13.5$ (d, $^2J_{P,P} = 30.5$ Hz, P_1), 18.3 (s, P_0), 51.6 (d, $^2J_{P,P} = 30.5$ Hz, P'_1), 63.4 (s, P_2) ppm. $C_{40}H_{42}Cl_4N_5O_5P_5S_3$ (1065.7): calcd. C 45.08, H 3.97, N 6.57; found C 44.89, H 3.91, N 6.51.

Dendron 6-G_2: Powdered hydroxybenzaldehyde sodium salt (0.043 g, 0.301 mmol, an excess) was added to a solution of **3-G_2** (0.073 g, 0.069 mmol) in THF (5 mL). The resulting mixture was stirred overnight at room temperature. This solution was centrifuged then evaporated to dryness. The resulting powder was washed with THF/pentane (1:10) to afford **6-G_2** as a white powder in 90% yield (0.087 g). ^1H NMR ($CDCl_3$): $\delta = 1.32$ (t, $^3J_{H,H} = 7.1$ Hz, 6 H, CH_2-CH_3), 3.38 (d, $^3J_{H,P} = 11.0$ Hz, 6 H, N-CH_3), 4.11 (dt, $^3J_{H,H} = 7.1$, $^3J_{H,P} = 15.0$ Hz, 4 H, CH_2), 6.35 (t, $^3J_{H,H} = {^2J_{H,P}} = 17.2$ Hz, 1 H, =CH-P_0), 7.19 (dd, $^3J_{H,H} = 8.7$, $^4J_{H,P} = 1.4$ Hz, 4 H, H-C_1^2), 7.37 (dd, $^3J_{H,H} = 8.5$, $^4J_{H,P} = 1.4$ Hz, 8 H, H-C_2^2), 7.57 (d, $^3J_{H,H} = 8.7$ Hz, 4 H, H-C_1^3), 7.85 (d, $^3J_{H,H} = 8.5$ Hz, 8 H, H-C_2^3), 7.40−7.74 (m, 17 H, H_{Arom}, CH=N, CH=CH), 9.92 (s, 4 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 16.27$ (d, $^3J_{C,P} = 6.1$ Hz, CH_2-CH_3), 32.56 (d, $^2J_{C,P} = 13.1$ Hz, N-CH_3), 62.05 (d, $^2J_{C,P} = 5.7$ Hz, CH_2), 117.48 (d, $^1J_{C,P} = 190.2$ Hz, =CH-P_0), 122.01 (br. d, $^3J_{C,P} = 4.0$ Hz, C_1^2, C_2^2), 127.28 (d, $^3J_{C,P} = 13.5$ Hz, C_0^3), 127.98 (s, C_1^3), 128.01 (dd, $^1J_{C,P} = 106.5$, $^3J_{C,P} = 5.0$ Hz, C_0^i), 128.49 (d, $^3J_{C,P} = 14.0$ Hz, C_0^m), 130.15 (dd, $^1J_{C,P} = 108.0$, $^3J_{C,P} = 3.9$ Hz, C_0^1), 130.40 (s, C_1^4), 131.26 (s, C_2^3), 132.65 (s, C_2^4), 132.68 (d, $^2J_{C,P} = 11.0$ Hz, C_0^o), 132.72 (s, C_0^p), 133.20 (d, $^2J_{C,P} = 15.0$ Hz, C_0^2), 138.51 (d, $^3J_{C,P} = 21.0$ Hz, C_0^4), 140.08 (d, $^3J_{C,P} = 16.0$ Hz, CH=N-N), 146.72 (d, $^2J_{C,P} = 6.0$ Hz, *C*H=CH-P_0), 153.12 (d, $^2J_{C,P} = 10.2$ Hz, C_1^1), 156.85 (d, $^2J_{C,P} = 9.8$ Hz, C_2^1), 190.92 (s, CHO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 13.7$ (d, $^2J_{P,P} = 29.2$ Hz, P_1), 18.2 (s, P_0), 51.8 (d, $^2J_{P,P} = 29.2$ Hz, P'_1), 60.7 (s, P_2) ppm. $C_{68}H_{62}N_5O_{13}P_5S_3$ (1408.3): calcd. C 57.99, H 4.44, N 4.97; found C 58.11, H 4.47, N 4.94.

Dendron 8-G_1: Dichloromethane (1 mL) was added to a mixture of powdered **3-G_0** (0.100 g, 0.236 mmol) and azide **7** (0.046 g, 0.236 mmol), to dissolve both reagents. The resulting solution was stirred for three days at room temperature. The solvent was evaporated to afford **8-G_1** in quantitative yield as a white powder (0.140 g). ^1H NMR ($CDCl_3$): $\delta = 1.28$ (t, $^3J_{H,H} = 7.0$ Hz, 6 H, CH_2-CH_3), 2.66 (d, $^3J_{H,P} = 11.9$ Hz, 6 H, N-CH_3), 3.56 (br. s, 4 H, NH_2), 4.06 (dt, $^3J_{H,H} = 7.0$, $^3J_{H,P} = 14.5$ Hz, 4 H, CH_2), 6.31 (t, $^3J_{H,H} = {^2J_{H,P}} = 17.2$ Hz, 1 H, =CH-P_0), 7.36−7.84 (m, 15 H, H_{Arom}, C*H*=CH-P_0) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 16.36$ (d, $^3J_{C,P} = 5.9$ Hz, CH_2-CH_3), 39.37 (d, $^2J_{C,P} = 6.0$ Hz, N-CH_3), 62.00 (d, $^2J_{C,P} = 5.7$ Hz, CH_2), 117.50 (d, $^1J_{C,P} = 190.5$ Hz, =CH-P_0), 127.53 (d, $^3J_{C,P} = 13.1$ Hz, C_0^3), 128.70 (d, $^3J_{C,P} = 12.2$ Hz, C_0^m), 129.40 (br. d, $^1J_{C,P} = 110.0$ Hz, C_0^i), 129.90 (d, $^1J_{C,P} = 110.0$ Hz, C_0^1), 132.54 (s, C_0^p), 132.62 (d, $^2J_{C,P} = 10.2$ Hz, C_0^o), 133.30 (d, $^2J_{C,P} = 11.5$ Hz, C_0^2), 138.46 (d, $^3J_{C,P} = 23.7$ Hz, C_0^4), 146.85 (d, $^2J_{C,P} = 6.7$ Hz, *C*H=CH-P_0) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 12.8$ (d, $^2J_{P,P} = 17.2$ Hz, P_1), 18.2 (s, P_0), 71.2 (d, $^2J_{P,P} = 17.2$ Hz, P'_1) ppm. $C_{26}H_{36}N_5O_3P_3S$ (591.59): calcd. C 52.79, H 6.13, N 11.84; found C 52.85, H 6.19, N 11.75.

Dendron 10-G_1: DMF (2 mL) was added to a mixture of powdered **8-G_1** (0.130 g, 0.219 mmol) and helicin **9** (0.125 g, 0.439 mmol). The resulting solution was stirred overnight then evaporated to dryness. **10-G_1** was isolated as an oil in quantitative yield (0.250 g). A strict stoichiometric amount of reagents must be used since it is difficult to eliminate the unreacted helicin. ^1H NMR ([D_8]THF): $\delta = 1.40$ (t, $^3J_{H,H} = 7.0$ Hz, 6 H, CH_2-CH_3), 3.28 (d, $^3J_{H,P} = 8.7$ Hz, 3 H, N-CH_3), 3.30 (d, $^3J_{H,P} = 8.7$ Hz, 3 H, N-CH_3), 3.41−3.92 (m, 12 H, CH_2 and CH helicin), 4.19 (dt, $^3J_{H,H} = 7.0$, $^3J_{H,P} = 15.0$ Hz, 4 H, CH_2OP), 4.74−5.11 (m, 10 H, OH, HC_1^7), 6.64 (t, $^3J_{H,H} = {^2J_{H,P}} = 17.2$ Hz, 1 H, =CH-P_0), 6.88 (m, 2 H, HC_1^3), 7.22 (m, 4 H, HC_1^4, HC_1^5), 7.56−8.11 (m, 19 H, H_{Arom}, C*H*=CH-P_0) ppm. $^{13}C\{^1H\}$ NMR ([D_8]THF): $\delta = 17.80$ (d, $^3J_{C,P} = 5.9$ Hz, CH_2-CH_3), 33.89 (d, $^2J_{C,P} = 9.8$ Hz, N-CH_3), 34.04 (d, $^2J_{C,P} = 9.8$ Hz, N-CH_3), 63.41 (d, $^2J_{C,P} = 5.7$ Hz, CH_2OP), 63.72 (s, CH_2OH), 72.20 (s, $C_1^{1\circ}$), 75.87 (s, C_1^8), 79.01 (s, C_1^9 or C_1^{11}), 79.42 (s, C_1^{11} or C_1^9), 104.28 (s, C_1^7), 104.70 (s, C_1^7), 119.24 (s, C_1^5), 119.61 (d, $^{1}J_{C,P}$ = 188.8 Hz, =CH-P_0), 119.74 (s, C_1^5), 124.13 (s, C_1^3), 124.30 (s, C_1^3), 127.43 (s, C_1^2), 129.21 (d, $^{3}J_{C,P}$ = 13.2 Hz, C_0^3), 129.42 (s, C_1^1), 129.86 (s, C_1^4), 130.20 (d, $^{3}J_{C,P}$ = 12.5 Hz, C_0^m), 132.18 (br. d, $^{1}J_{C,P}$ = 108.3 Hz, C_0^i), 132.24 (d, $^{3}J_{C,P}$ = 14.2 Hz, CH=N), 132.44 (d, $^{1}J_{C,P}$ = 110.0 Hz, C_0^1), 133.94 (s, C_0^p), 134.98 (d, $^{2}J_{C,P}$ = 10.8 Hz, C_0^o), 133.50 (d, $^{2}J_{C,P}$ = 10.6 Hz, C_0^2), 140.47 (d, $^{3}J_{C,P}$ = 23.6 Hz, C_0^4), 148.86 (d, $^{2}J_{C,P}$ = 6.7 Hz, *C*H=CH-P_0), 157.37 (s, C_1^6), 157.52 (s, C_1^6) ppm. $^{31}P\{^{1}H\}$ NMR ([D_8]THF): δ = 14.6 (d, $^{2}J_{P,P}$ = 26.6 Hz, P_1), 24.0 (s, P_0), 62.5 (d, $^{2}J_{P,P}$ = 26.6 Hz, P'_1) ppm. $C_{52}H_{64}N_5O_{15}P_3S$ (1124.08): calcd. C 55.56, H 5.74, N 6.23; found C 55.47, H 5.71, N 6.31.

Cationic Dendron 11-G$_1$: Methyl trifluoromethanesulfonate (50 µL, 0.470 mmol) was added dropwise to a solution of **3-G$_1$** (0.350 g, 0.470 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred for 10 minutes at 0 °C and 20 minutes at room temperature and then evaporated to dryness. The crude residue was washed with pentane to afford **11-G$_1$** as a sticky yellow oil in 95% yield (0.405 g). ^{1}H NMR (CD_2Cl_2): δ = 1.30 (t, $^{3}J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 2.63 (d, $^{3}J_{H,P}$ = 18.2 Hz, 3 H, P_1-S-CH_3), 4.16 (dt, $^{3}J_{H,H}$ = 7.2, $^{3}J_{H,P}$ = 14.5 Hz, 4 H, CH_2), 6.55 (t, $^{3}J_{H,H}$ = $^{2}J_{H,P}$ = 17.0 Hz, 1 H, =CH-P_0), 7.24−8.07 (m, 23 H, H_{Arom}, C*H*=CH-P_0), 9.95 (s, 2 H, CHO) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ = 14.23 (d, $^{2}J_{C,P}$ = 5.3 Hz, S-CH_3), 16.62 (d, $^{2}J_{C,P}$ = 5.8 Hz, CH_3), 63.20 (br. s, CH_2), 121.28 (q, $^{1}J_{C,F}$ = 323.5 Hz, CF_3), 121.81 (d, $^{3}J_{C,P}$ = 4.9 Hz, C_1^2), 122.15 (d, $^{1}J_{C,P}$ = 186.2 Hz, =CH-P_0), 124.17 (dd, $^{1}J_{C,P}$ = 107.4, $^{3}J_{C,P}$ = 4.4 Hz, C_0^i), 126.03 (dd, $^{1}J_{C,P}$ = 101.7, $^{3}J_{C,P}$ = 5.8 Hz, C_0^1), 129.18 (d, $^{3}J_{C,P}$ = 12.8 Hz, C_0^3), 130.31 (d, $^{3}J_{C,P}$ = 13.5 Hz, C_0^m), 132.39 (s, C_1^3), 132.62 (d, $^{2}J_{C,P}$ = 11.7 Hz, C_0^o), 133.32 (d, $^{2}J_{C,P}$ = 12.0 Hz, C_0^2), 135.24 (d, $^{4}J_{C,P}$ = 2.9 Hz, C_0^p), 135.46 (s, C_1^4), 141.07 (d, $^{3}J_{C,P}$ = 26.4 Hz, C_0^4), 146.42 (br. s, *C*H=CH-P_0), 153.55 (d, $^{2}J_{C,P}$ = 10.9 Hz, C_1^1), 190.82 (s, CHO) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ = 16.9 (s, P_0), 22.2 (d, $^{2}J_{P,P}$ = 20.5 Hz, P_1), 23.1 (d, $^{2}J_{P,P}$ = 20.5 Hz, P'_1) ppm. $C_{40}H_{39}F_3NO_{10}P_3S_2$ (907.79): calcd. C 52.92, H 4.33, N 1.54; found C 53.21, H 4.42, N 1.48.

Dicationic Dendron (12-G$_1$): Trimethylsilyl trifluoromethanesulfonate (85 µL, 0.470 mmol) was added dropwise to a solution of **11-G$_1$** (0.420 g, 0.470 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred for 10 minutes at 0 °C and 30 minutes at room temperature and then evaporated to dryness. The crude residue was washed with pentane to afford **12-G$_1$** as a sticky yellow oil in 89% yield (0.473 g). ^{1}H NMR (CD_2Cl_2): δ = 0.10 (s, 9 H, $SiMe_3$), 1.47 (t, $^{3}J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 2.62 (d, $^{3}J_{H,P}$ = 18.2 Hz, 3 H, P_1-S-CH_3), 4.40 (dt, $^{3}J_{H,H}$ = 7.2, $^{3}J_{H,P}$ = 14.6 Hz, 4 H, CH_2), 6.73 (t, $^{3}J_{H,H}$ = $^{2}J_{H,P}$ = 17.0 Hz, 1 H, =CH-P_0), 7.24−8.07 (m, 23 H, H_{Arom} and C*H*=CH-P_0), 10.03 (s, 2 H, CHO) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ = 1.93 (s, $SiMe_3$), 14.21 (d, $^{2}J_{C,P}$ = 5.3 Hz, S-CH_3), 16.19 (d, $^{2}J_{C,P}$ = 5.8 Hz, CH_3), 66.97 (d, $^{2}J_{C,P}$ = 5.4 Hz, CH_2), 113.32 (d, $^{1}J_{C,P}$ = 194.2 Hz, =CH-P_0), 120.58 (q, $^{1}J_{C,F}$ = 323 Hz, CF_3), 121.77 (d, $^{3}J_{C,P}$ = 4.8 Hz, C_1^2), 123.56 (dd, $^{1}J_{C,P}$ = 106.9, $^{3}J_{C,P}$ = 4.1 Hz, C_0^i), 126.67 (dd, $^{1}J_{C,P}$ = 107.5, $^{3}J_{C,P}$ = 4.0 Hz, C_0^1), 129.85 (d, $^{3}J_{C,P}$ = 13.8 Hz, C_0^3), 130.33 (d, $^{3}J_{C,P}$ = 13.6 Hz, C_0^m), 132.41 (s, C_1^3), 132.62 (d, $^{2}J_{C,P}$ = 11.9 Hz, C_0^o), 133.26 (d, $^{2}J_{C,P}$ = 12.0 Hz, C_0^2), 135.31 (d, $^{4}J_{C,P}$ = 3.0 Hz, C_0^p), 135.52 (s, C_1^4), 139.78 (d, $^{3}J_{C,P}$ = 28.6 Hz, C_0^4), 151.19 (d, $^{2}J_{C,P}$ = 8.9 Hz, *C*H=CH-P_0), 153.52 (d, $^{2}J_{C,P}$ = 10.9 Hz, C_1^1), 190.83 (s, CHO) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ = 22.0 (d, $^{2}J_{P,P}$ = 20.7 Hz, P_1), 23.2 (d, $^{2}J_{P,P}$ = 20.7 Hz, P'_1), 23.6 (s, P_0) ppm. $C_{44}H_{48}F_6NO_{13}P_3S_3Si$ (1130.1): calcd. C 46.77, H 4.28, N 1.24; found C 46.94, H 4.32, N 1.15.

Dendron 14-G$_2$: THF (8 mL) was added to a powdered mixture of **3-G$_2$** (0.055 g, 0.0516 mmol), compound **13** (0.086 g, 0.227 mmol, slight excess) and Cs_2CO_3 (0.150 g, 0.454 mmol, excess). The resulting mixture was stirred overnight then centrifuged, and the solution was evaporated to dryness. The resulting powder was washed with THF/pentane to eliminate unreacted **7**. Compound **14-G$_2$** was obtained as a white powder in 63% yield (0.081 g). ^{1}H NMR ($CDCl_3$): δ = 1.33 (t, $^{3}J_{H,H}$ = 7.1 Hz, 6 H, CH_2−C*H*$_3$), 3.33 (d, $^{3}J_{H,P}$ = 10.5 Hz, 6 H, N-CH_3), 4.12 (dt, $^{3}J_{H,H}$ = 7.1, $^{3}J_{H,P}$ = 14.8 Hz, 4 H, CH_2), 6.37 (t, $^{3}J_{H,H}$ = $^{2}J_{H,P}$ = 17.1 Hz, 1 H, =CH-P_0), 6.86 (d, $^{3}J_{H,H}$ = 8.1 Hz, 8 H, H-C_2^3), 6.92 (m, 4 H, H-C_3^3), 7.15 (d, $^{3}J_{H,H}$ = 8.1 Hz, 8 H, H-C_2^2), 7.23−7.78 (m, 73 H, H_{Arom}, CH=N, CH=CH), 8.15 (br. dd, $^{3}J_{H,H}$ = 6.9, $^{4}J_{H,P}$ = 4.1 Hz, 4 H, H-C_3^6), 9.02 (d, $^{4}J_{H,P}$ = 5.1 Hz, 1 H, CH=N-C) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 16.28 (d, $^{3}J_{C,P}$ = 6.0 Hz, CH_2−*C*H$_3$), 32.96 (d, $^{2}J_{C,P}$ = 13.1 Hz, N-CH_3), 61.94 (d, $^{2}J_{C,P}$ = 5.5 Hz, CH_2), 117.53 (d, $^{1}J_{C,P}$ = 189.0 Hz, =CH-P_0), 121.84 (br. s, C_1^2, C_2^2, C_2^3), 127.18 (d, $^{3}J_{C,P}$ = 13.3 Hz, C_0^3), 127.85 (s, C_1^3), 127.99 (d, $^{3}J_{C,P}$ = 14.2 Hz, C_0^m), 128.01 (dd, $^{1}J_{C,P}$ = 106.0, $^{3}J_{C,P}$ = 6.0 Hz, C_0^i), 128.17 (d, $^{3}J_{C,P}$ = 3.9 Hz, C_3^6), 128.52 (d, $^{3}J_{C,P}$ = 7.1 Hz, C_3^m), 128.79 (br. s, C_3^5, C_3^p), 130.10 (dd, $^{1}J_{C,P}$ = 108.0, $^{3}J_{C,P}$ = 3.6 Hz, C_0^1), 130.77 (s, C_3^4), 130.90 (s, C_1^4), 132.58 (d, $^{2}J_{C,P}$ = 11.0 Hz, C_0^o), 132.70 (s, C_0^p), 133.30 (d, $^{2}J_{C,P}$ = 15.3 Hz, C_0^2), 133.44 (s, C_3^3), 133.88 (d, $^{2}J_{C,P}$ = 19.9 Hz, C_3^o), 136.24 (d, $^{1}J_{C,P}$ = 8.7 Hz, C_3^i), 138.46 (d, $^{2}J_{C,P}$ = 20.4 Hz, C_3^1), 138.53 (d, $^{3}J_{C,P}$ = 21.0 Hz, C_0^4), 138.84 (d, $^{1}J_{C,P}$ = 17.3 Hz, C_3^2), 139.07 (br. d, $^{3}J_{C,P}$ = 13.5 Hz, CH=N-N), 146.68 (d, $^{2}J_{C,P}$ = 6.5 Hz, *C*H=CH-P_0), 148.54 (d, $^{2}J_{C,P}$ = 5.9 Hz, C_2^1), 148.55 (s, C_2^4), 152.92 (d, $^{2}J_{C,P}$ = 10.2 Hz, C_1^1), 158.62 (d, $^{3}J_{C,P}$ = 20.9 Hz, *C*H=N-C) ppm. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = −13.1 (s, P_3), 13.5 (d, $^{2}J_{P,P}$ = 30.5 Hz, P_1), 18.3 (s, P_0), 51.8 (d, $^{2}J_{P,P}$ = 30.5 Hz, P'_1), 63.5 (s, P_2) ppm. $C_{140}H_{118}N_9O_9P_9S_3$ (2445.5): calcd. C 68.76, H 4.86, N 5.16; found C 68.64, H 4.82, N 5.11.

Complexed Dendron (15-G$_2$): A solution of **14-G$_2$** (0.200 g, 0.082 mmol) in CH_2Cl_2 (25 mL) was added slowly dropwise during 2 hours to a solution of [$PdCl_2$(COD)] (0.093 g, 0.327 mmol) in CH_2Cl_2 (25 mL). The resulting solution was stirred for 3 hours more then evaporated to dryness. The residue was washed with THF/pentane (1:10) to afford **15-G$_2$** as a pale yellow powder in 85% yield (0.219 g). ^{1}H NMR (CD_2Cl_2): δ = 1.30 (t, $^{3}J_{H,H}$ = 7.0 Hz, 6 H, CH_2−C*H*$_3$), 3.31 (d, $^{3}J_{H,P}$ = 10.7 Hz, 6 H, N-CH_3), 4.07 (m, 4 H, CH_2), 6.41 (t, $^{3}J_{H,H}$ = $^{2}J_{H,P}$ = 17.2 Hz, 1 H, =CH-P_0), 7.07 (m, 4 H, H-C_3^3), 7.16 (d, $^{3}J_{H,H}$ = 8.8 Hz, 8 H, H-C_2^3), 7.28 (d, $^{3}J_{H,H}$ = 8.8 Hz, 8 H, H-C_2^2), 7.40−7.80 (m, 73 H, H_{Arom}, CH=N, CH=CH), 7.93 (m, 4 H, H-C_3^6), 8.21 (d, $^{4}J_{H,P}$ = 5.1 Hz, 1 H, CH=N-C) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ = 16.79 (d, $^{3}J_{C,P}$ = 5.9 Hz, CH_2−*C*H$_3$), 33.58 (d, $^{2}J_{C,P}$ = 13.1 Hz, N-CH_3), 62.59 (d, $^{2}J_{C,P}$ = 6.0 Hz, CH_2), 118.58 (d, $^{1}J_{C,P}$ = 189.1 Hz, =CH-P_0), 121.94 (d, $^{2}J_{C,P}$ = 3.8 Hz, C_2^2), 122.45 (d, $^{2}J_{C,P}$ = 5.3 Hz, C_1^2), 122.23 (d, $^{1}J_{C,P}$ = 49.4 Hz, C_3^2), 125.09 (s, C_2^3), 125.69 (d, $^{1}J_{C,P}$ = 61.1 Hz, C_3^i), 128.20 (d, $^{3}J_{C,P}$ = 13.7 Hz, C_0^3, C_0^m), 128.64 (br. s, C_1^3, C_3^6), 128.72 (dd, $^{1}J_{C,P}$ = 106.0, $^{3}J_{C,P}$ = 3.5 Hz, C_0^i), 129.26 (s, C_3^5), 129.58 (d, $^{3}J_{C,P}$ = 13.0 Hz, C_3^m), 131.50 (dd, $^{1}J_{C,P}$ = 106.0, $^{3}J_{C,P}$ = 4.0 Hz, C_0^1), 131.63 (s, C_1^4), 133.12 (d, $^{4}J_{C,P}$ = 5.5 Hz, C_3^p), 133.32 (s, C_3^4), 133.69 (d, $^{2}J_{C,P}$ = 13.2 Hz, C_0^o), 133.79 (s, C_0^p), 134.00 (d, $^{2}J_{C,P}$ = 16.0 Hz, C_0^2), 134.40 (s, C_3^3), 134.68 (d, $^{2}J_{C,P}$ = 10.9 Hz, C_3^o), 137.14 (d, $^{2}J_{C,P}$ = 15.9 Hz, C_3^1), 139.23 (d, $^{3}J_{C,P}$ = 21.0 Hz, C_0^4), 140.83 (d, $^{3}J_{C,P}$ = 12.8 Hz, CH=N-N), 146.99 (d, $^{2}J_{C,P}$ = 6.4 Hz, *C*H=CH-P_0), 149.77 (s, C_2^4), 150.34 (d, $^{2}J_{C,P}$ = 5.9 Hz, C_2^1), 153.59 (d, $^{2}J_{C,P}$ = 9.8 Hz, C_1^1), 166.7 (d, $^{3}J_{C,P}$ = 9.1 Hz, *C*H=N-C) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ = 15.6 (d, $^{2}J_{P,P}$ = 29.1 Hz, P_1), 19.7 (s, P_0), 33.0 (s, P_3), 53.2 (d, $^{2}J_{P,P}$ = 29.1 Hz, P'_1), 64.8 (s, P_2) ppm. $C_{140}H_{118}Cl_8N_9O_9P_9Pd_4S_3$ (3154.8): calcd. C 53.30, H 3.77, N 4.00; found C 53.38, H 3.82, N 4.02.

X-ray Crystallographic Study: Data collection was performed on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an

Oxford Cryosystems Cryostream Cooler. Device and using a graphite-monochromated Mo-K_α radiation (λ = 0.71073Å), at T = 160 K. Further details are provided in Table 1. Final unit-cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections, and crystal decay was monitored during the data collection by measuring 200 reflections by exposure. No significant fluctuations of the intensities were observed during measurement.

Table 1. Crystal data, data collection and structure refinement

Empirical formula	$C_{24}H_{26}O_3P_2$
Molecular mass	424.39
Wavelength	0.71073Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a = 15.435(2) Å b = 8.6930(11) Å c = 16.326(3) Å α = 90.179(17)° β = 92.141(18)° γ = 90.067(16)°
Volume	2189.1(5) Å^3
Z, calculated density	4, 1.288 mg/m^3
Absorption coefficient	0.221 mm^{-1}
F(000)	896
Crystal size	0.42 × 0.17 × 0.08 mm
Crystal colour and form	colourless plate
Tube power	1.50 kW
Tube voltage	50 kV
Tube current	30 mA
Collimator size	0.8 mm
Detector distance	70.0 mm
2θ range	3.3−52.1°
d(hkl) range	12.453−0.809 Å
φ movement mode	rotation
φ start	0.0°
φ end	200.2°
φ increment	1.1°
Number of exposures	182
Irradiation/exposure	2.00 min
Measurement duration	19 h
θ range for data collection	2.64−23.26°
Index ranges	$-17 \leq h \leq 17$ $-9 \leq k \leq 9$ $-18 \leq l \leq 18$
Reflections collected/unique	12240/3099 [R(int) = 0.0592]
Completeness to 2θ = 46.52	98.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3099/0/272
Goodness-of-fit on F^2	1.032
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0509P)^2 + 1.396P]$ where $P = (F_o^2 + 2F_c^2)/3$
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0377, $wR2$ = 0.0979
R indices (all data)	$R1$ = 0.0413, $wR2$ = 0.1011
Largest diff. peak and hole	(0.705 and −0.364) e·Å^{-3}

The structure was solved by means of direct methods using the program SIR92[31] and subsequent difference Fourier maps, then refined by least-squares procedures on F^2 by using the program SHELXL-97.[32] Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[33]

All hydrogen atoms were located in difference Fourier maps, but introduced in the refinement as fixed contributors by using a riding model with an isotropic thermal parameter fixed at 20% higher than those of the C_{sp^2} atoms and 50% for the C_{sp^3} atoms to which they are connected, excepted hydrogens atoms labelled H(1) and H(2) attached to the C(1) and C(2) carbons atoms, respectively, which were refined isotropically. Methyl groups were refined with the torsion angle as a free variable. All non-hydrogen atoms were refined anisotropically, and in the last cycles of refinement weighting schemes were used. The weights were calculated from the following formula: $W = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Criteria for a satisfactory complete analysis were the ratios of root-mean-square shift standard deviation being less than 0.1 and no significant features in the final difference Fourier maps. Drawings of the molecules were produced with the program ORTEP3[34] with 50% probability displacement ellipsoids for non-hydrogen atoms.

CCDC-228136 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

---

[1] G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons*, Wiley-VCH, Weinheim (Germany), **2001**.

[2] J. M. J. Fréchet, D. A. Tomalia, *Dendrimers and other Dendritic Polymers*, Wiley Europe, Chichester, **2001**.

[3] C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638−7647.

[4] V. Maraval, R. Laurent, B. Donnadieu, M. Mauzac, A. M. Caminade, J. P. Majoral, *J. Am. Chem. Soc.* **2000**, *122*, 2499−2511.

[5] K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4252−4261.

[6] D. C. Tully, J. M. J. Fréchet, *Chem. Commun.* **2001**, 1229−1239.

[7] P. Savignac, B. Iorga, *Modern Phosphonate Chemistry*, CRC Press, **2003**.

[8] V. Maraval, D. Prévôté-Pinet, R. Laurent, A. M. Caminade, J. P. Majoral, *New J. Chem.* **2000**, *24*, 561−566.

[9] V. Maraval, R. M. Sebastian, F. Ben, R. Laurent, A. M. Caminade, J. P. Majoral, *Eur. J. Inorg. Chem.* **2001**, 1681−1691.

[10] J. P. Majoral, A. M. Caminade, *Chem. Rev.* **1999**, *99*, 845−880.

[11] M. L. Lartigue, B. Donnadieu, C. Galliot, A. M. Caminade, J. P. Majoral, J. P. Fayet, *Macromolecules* **1997**, *30*, 7335−7337.

[12] M. L. Lartigue, N. Launay, B. Donnadieu, A. M. Caminade, J. P. Majoral, *Bull. Soc. Chim. Fr.* **1997**, *134*, 981−988.

[13] C. Galliot, C. Larré, A. M. Caminade, J. P. Majoral, *Science* **1997**, *277*, 1981−1984.

[14] G. M. Salamonczyk, M. Kuznikowski, E. Poniatowska, *Tetrahedron Lett.* **2002**, *43*, 1747−1749.

[15] B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863−927.

[16] D. Prévôté, S. Le Roy-Gourvennec, A. M. Caminade, S. Masson, J. P. Majoral, *Synthesis* **1997**, 1199−1207.

[17] C. Larré, A. M. Caminade, J. P. Majoral, *Angew. Chem.* **1997**, *109*, 614−617; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 596−599.

[18] N. Launay, A. M. Caminade, R. Lahana, J. P. Majoral, *Angew. Chem.* **1994**, *106*, 1682−1684; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1589−1592.

[19] N. Launay, A. M. Caminade, J. P. Majoral, *J. Am. Chem. Soc.* **1995**, *117*, 3282−3283.

[20] V. Maraval, R. Laurent, S. Merino, A. M. Caminade, J. P. Majoral, *Eur. J. Org. Chem.* **2000**, 3555−3568.

[21] R. M. Sebastian, G. Magro, A. M. Caminade, J. P. Majoral, *Tetrahedron* **2000**, *56*, 6269−6277.

[22] G. Magro, B. Donnadieu, A. M. Caminade, J. P. Majoral, *Chem. Eur. J.* **2003**, *9*, 2151−2159.

[23] C. Larré, B. Donnadieu, A. M. Caminade, J. P. Majoral, *J. Am.*

Chem. Soc. **1998**, *120*, 4029−4030.
[24] F. Gonce, A. M. Caminade, J. P. Majoral, *Tetrahedron Lett.* **1991**, *32*, 203−206.
[25] J. P. Majoral, M. Badri, A. M. Caminade, M. Delmas, A. Gaset, *Inorg. Chem.* **1991**, *30*, 344−346.
[26] M. Koprowski, R. M. Sebastian, V. Maraval, M. Zablocka, V. Cadierno-Menendez, B. Donnadieu, A. Igau, A. M. Caminade, J. P. Majoral, *Organometallics* **2002**, *21*, 4680−4687.
[27] G. Guerrero, P. H. Mutin, A. Vioux, *J. Mater. Chem.* **2001**, *11*, 3161−3165.
[28] G. Guerrero, P. H. Mutin, A. Vioux, *Chem. Mater.* **2001**, *13*, 4367−4373.
[29] G. P. Schiemenz, H. Kaack, *Justus Liebigs Ann. Chem.* **1973**, *9*, 1480−1493.
[30] J. Mitjaville, A. M. Caminade, R. Mathieu, J. P. Majoral, *J. Am. Chem. Soc.* **1994**, *116*, 5007−5008.
[31] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343−350.
[32] G. M. Sheldrick, *SHELX97 − Programs for Crystal Structure Analysis* (Release 97-2). Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, Germany, **1998**.
[33] *International Tables for X-ray Crystallography*, Vol IV, Kynoch press, Birmingham, England, **1974**.
[34] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

Received January 10, 2004
Early View Article