

Rapid Synthesis of Phosphorus-Containing Dendrimers with Controlled Molecular Architectures: First Example of Surface-Block, Layer-Block, and Segment-Block Dendrimers Issued from the Same Dendron

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Abstract: A third generation dendron possessing one activated vinyl group linked to the core and 16 chlorines linked to the surface has been functionalized with various groups at the core (primary amine, phosphine, or azide), and on the surface (aldehyde, tertiary amine, or nitrile). These functionalized dendrons are used as building blocks for the synthesis of several complex dendritic architectures, obtained through core–core, core–surface, or core–core–surface–core couplings using very simple one-step reactions between these functions, such as Michael additions between vinyl and primary amino groups or Staudinger reactions between phosphines and azides. These reactions finally induce the formation of layer-block dendrons, a surface-block dendrimer, a layer-block dendrimer, a layered surface-block dendrimer, and a segment-block dendrimer, all issued from the same original dendron.

Introduction

Dendrimers constitute a new class of macromolecules which has strongly stirred up the imagination of the scientific community for more than 10 years. Indeed, these highly branched nanosized macromolecules possess precise constitutions and a large number of functional groups which confer upon them unique properties.¹ In fact, the main drawback of these fascinating molecules is their lengthy step-by-step synthesis. A few ways to improve this synthetic pathway have been proposed, most of them implying molecular trees called “dendrons”.² The dendrons are reminiscent of dendrimers, but in contrast to dendrimers, they possess one reactive function at the level of the core. Most of these dendrons are obtained by a convergent strategy introduced by Fréchet³ and are synthesized in most cases only up to generation 2, 3, or 4, to avoid the steric crowding of the core function. Depending on the type of this function, several dendrons can be associated by their core in a spontaneous self-assembly,⁴ around a metal,⁵ or by reaction with

a multifunctional core,⁶ which may be a small dendrimer. The grafting of dendrons on dendrimers allows to increase dramatically the number of end groups of the dendrimer in one step, for instance from 6 to 96⁷ or from 12 to 288,⁸ creating “layer-block” dendrimers⁹ (Figure 1). This way has been also applied

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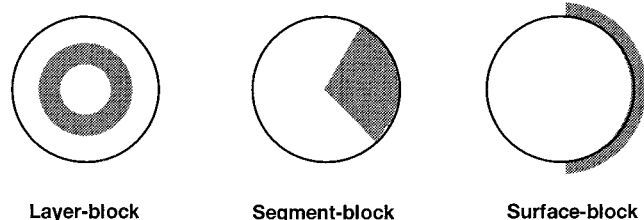


Figure 1. Schematized special dendritic architectures.

to the rapid synthesis of dendrons. In these cases, the surface of one dendron reacts with the core of several dendrons.¹⁰ Association of these larger dendrons by their core is another way to obtain layer-block dendrimers when layered dendrons are used.¹¹

Interestingly, very special macromolecular architectures called “segment-block” or “surface-block” dendrimers⁹ (Figure 1) have been obtained mainly using dendrons. In the first case, several different types of dendrons are associated, either two generations or more of the same dendron,¹² or the same generation with a different skeleton to obtain segment-block dendrimers.¹³ Surface-block dendrimers possess two different types of end groups located in definite areas on the surface of the dendrimers; they are obtained by grafting dendrons with different end groups together or on a single core. The ratio of both surface groups depends on the relative amount of each type of dendrons¹⁴ or on the generation used for both dendrons, which may be different.¹⁵

To the best of our knowledge, no example of synthesis of all these special dendritic architectures (layer-block, segment-block, and surface-block dendrimers), using only subtle modifications of a unique dendron in the last step of its synthesis has been described up to now. However, such an approach is particularly interesting, because it would dramatically fasten the synthesis of special dendritic architectures. Pursuing our researches concerning tailored dendrimers,¹⁶ we reasoned that the divergent method we used to synthesize phosphorus-containing dendrimers¹⁷ could be applied to the synthesis of dendrons. The advantage of the divergent method over the convergent one is

that the surface is always very easily functionalized.¹⁸ Thus, our aim was to prepare a dendron possessing one function located at the core and several easily reactive functions located on the surface. We report here the synthesis of a third generation phosphorus-containing dendron possessing a vinyl group at the level of the core and 16 chlorines on the surface, its subsequent functionalization at both levels independently, and the use of such functionalized dendrons as building blocks for the synthesis of surface-block, layer-block, and segment-block dendrimers.

Results and Discussion

The main difficulty in using the divergent strategy for the synthesis of dendrons is to keep unreacted the function located at the level of the core when growing the dendron and then to activate it later. The function we choose to place at the core is an activated vinyl group which should undergo Michael type reactions with amines, but which should not react during the synthesis of the dendron. The first step of this synthesis is a Staudinger reaction between diphenylvinylphosphine and several functionalized phosphorus azides **1a–d** (Scheme 1). Azides **1a–c** were obtained reacting one equivalent of P(SiCl₃), first with two equivalents of functionalized phenols in basic conditions at low temperature and then with NaN₃. An X-ray structure analysis of compound **1b** (Figure 2) indicates that the bond lengths and bond angles of the P–N–N–N linkage compare well with those found for other phosphorus azides.¹⁹

The Staudinger reaction induces the quantitative formation of compounds **2a–d**–[G'₀], possessing a P=N–P=S linkage, characterized in ³¹P NMR by the appearance of two doublets. The X-ray structure analysis of compound **2c**–[G'₀] reveals the presence of two crystallographically independent molecules. The ZORTEP drawing of one of them (**2c**–[G'₀a]) is represented in Figure 3. Bond lengths and angles of the P=N–P=S linkage in both molecules are similar to those we already reported,²⁰ as well as to those concerning the P–CH=CH₂ group.²¹

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Scheme 1

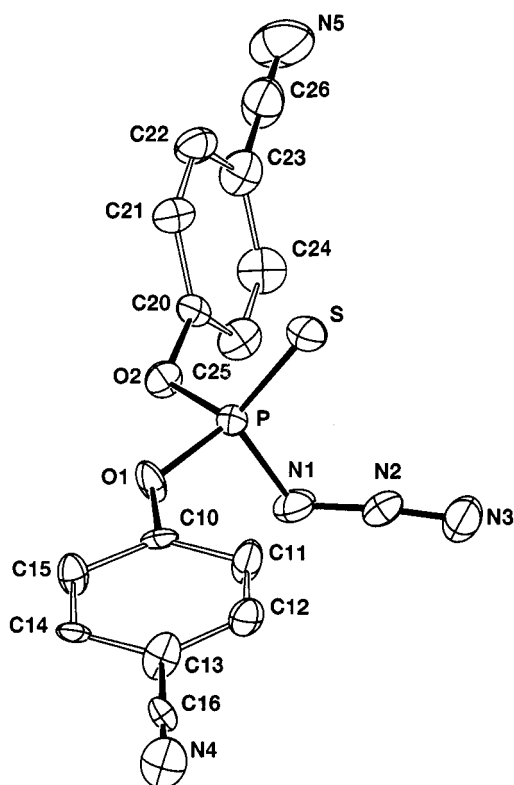
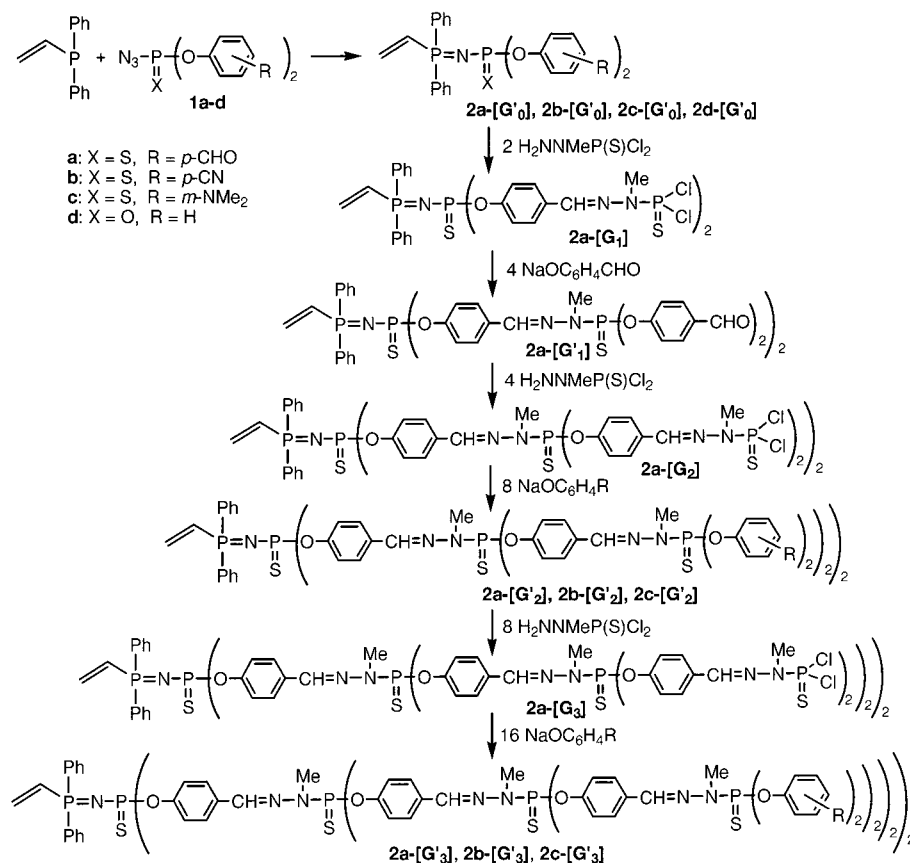


Figure 2. ZORTEP drawing of compound **1b**. Selected bond lengths in Å and bond angles in degrees: P–N1 1.690(11); N1–N2 1.242(14); N2–N3 1.119(13); P–N1–N2 117.2(9); N1–N2–N3 173.6(12).

Compounds **2b–d-[G'_0]** have been synthesized as models to test the functionalization at the level of the core (see examples later on), but only compound **2a-[G'_0]** can be used to grow the

dendron. The next step for this purpose is the reaction of **2a-[G'_0]** with $\text{H}_2\text{NNMeP(S)Cl}_2$. The expected reaction was the condensation of the NH_2 group with the aldehyde, but a Michael addition of the NH_2 on the vinyl group could not be ruled out. In fact, the condensation reaction is faster than the Michael addition of the primary amino group, and we have never observed this addition, even when a slight excess of $\text{H}_2\text{NNMeP(S)Cl}_2$ is used. The condensation induces the formation of compound **2a-[G_1]**, characterized by the disappearance of the signals corresponding to the CHO groups in ^1H NMR and IR, as well as the disappearance of both doublets in ^{31}P NMR ($\delta = 10.6$ and 50.9 ppm for **2a-[G'_0]**) on behalf of the appearance of two new doublets ($\delta = 11.8$ and 52.7 ppm for **2a-[G_1]**) for the P=N–P=S linkage. The presence of the unreacted vinyl group is indicated by ^1H NMR (ABCX system) and ^{13}C NMR ($\delta = 136.9$ for $\text{CH}_2=$). The structure of compound **2a-[G_1]** is confirmed by an X-ray structure analysis (Figure 4). The data concerning the $\text{CH}_2=\text{CH}-\text{P}=\text{N}-\text{P}=\text{S}$ linkage of **2a-[G_1]** compare well with those of **2c-[G'_0]**. One can notice also that each arm (the $\text{OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}(\text{Me})\text{P}=\text{S}$ linkage) is flat, a tendency which was already seen for other small dendrimers possessing this linkage.^{16c–e,17d}

Dendrons **2a-[G_n]** are grown from **2a-[G_1]**, using the method we already described for the synthesis of dendrimers,¹⁷ alternating addition of hydroxybenzaldehyde sodium salt and $\text{H}_2\text{NNMeP(S)Cl}_2$. These reactions are carried out up to the formation of the third generation dendron **2a-[G_3]** (Scheme 1), possessing 16 chlorines on the surface and one vinyl group located at the core. All of the steps preceding the synthesis of **2a-[G_3]** are monitored by ^{31}P NMR: a shielding of the signal of the phosphorus which undergoes the reaction is observed on going from $-\text{P(S)Cl}_2$ to $-\text{P(S)[OC}_6\text{H}_4\text{CHO}]_2$ (from $\delta \sim 63.3$ to $\delta \sim 60.5$ ppm), and a slight deshielding occurs for the signal

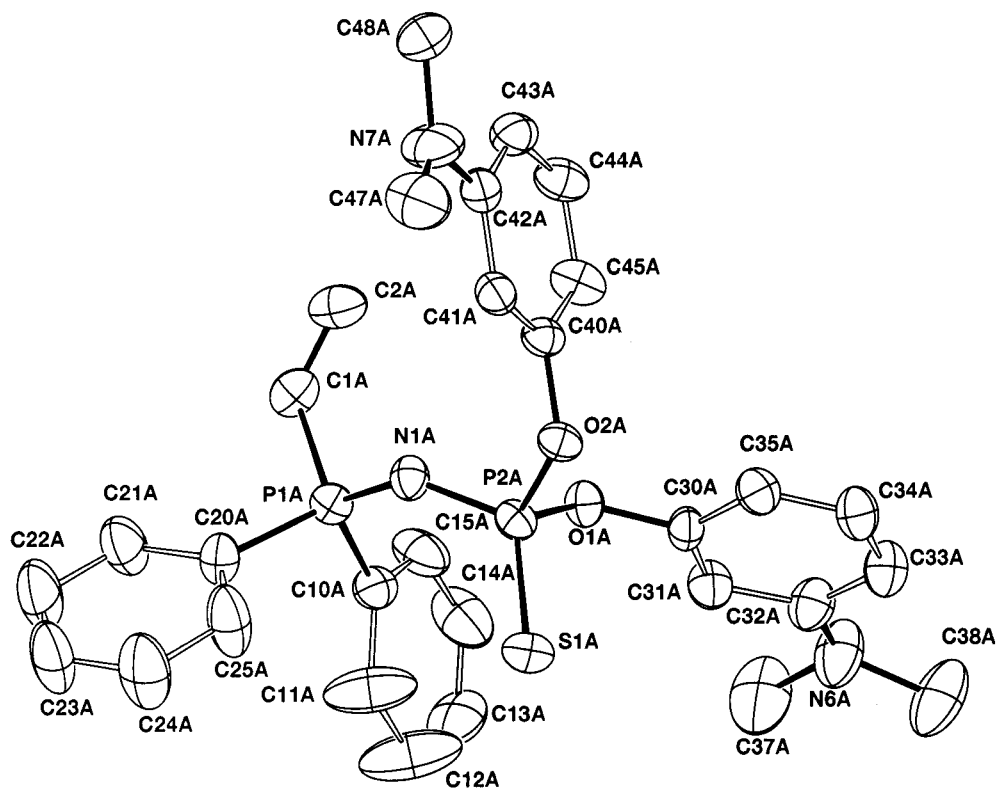


Figure 3. ZORTEP drawing of compound **2c**-[G'_{0a}]. Selected bond lengths in Å and bond angles in degrees for **2c**-[G'_{0a}] {and **2c**-[G'_{0b}]}; P2A–N1A 1.569(4), {P2B–N1B 1.590(4)}; N1A–P1A 1.569(4), {N1B–P1B 1.573(3)}; P1A–C1A 1.775(5), {P1B–C1B 1.780(5)}; C1A–C2A 1.308(7), {C1B–C2B 1.304(7)}; P2A–N1A–P1A 135.4(2), {P2B–N1B–P1B 132.4(2)}; N1A–P1A–C1A 110.2(2), {N1B–P1B–C1B 109.5(2)}; P1A–C1A–C2A 121.3(4), {P1B–C1B–C2B 121.6(4)}.

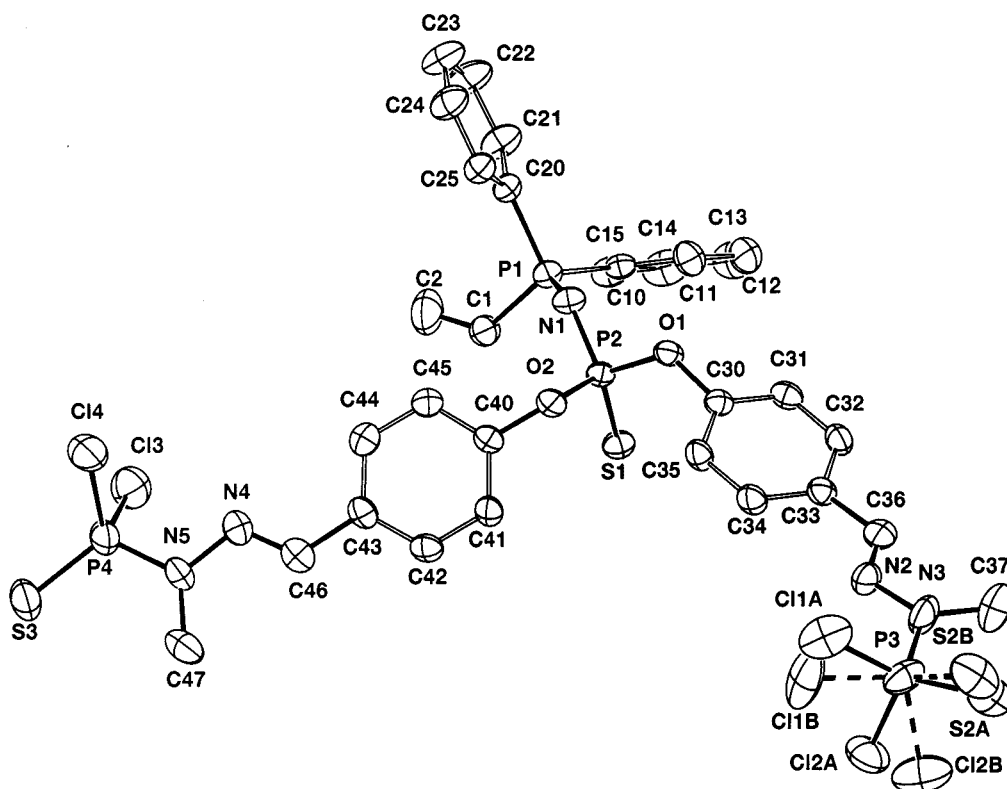


Figure 4. ZORTEP drawing of compound **2a**-[G₁] (one P(S)Cl₂ group is disordered). Selected bond lengths lengths in Å and bond angles in degrees: P2–N1 1.579(4); N1–P1 1.591(4); P1–C1 1.786(5); C1–C2 1.282(7); P2–N1–P1 127.4(2); N1–P1–C1 113.2(2); P1–C1–C2 127.1(4).

of the same phosphorus on going from $-\text{P}(\text{S})[\text{OC}_6\text{H}_4\text{CHO}]_2$ to $-\text{P}(\text{S})[\text{OC}_6\text{H}_4\text{CH}=\text{NNMeP}(\text{S})\text{Cl}_2]_2$ (from $\delta \sim 60.5$ to $\delta \sim 62.3$

ppm). Obviously, the condensation is also characterized by ^1H , ^{13}C NMR, and IR spectroscopies. It is important to note that

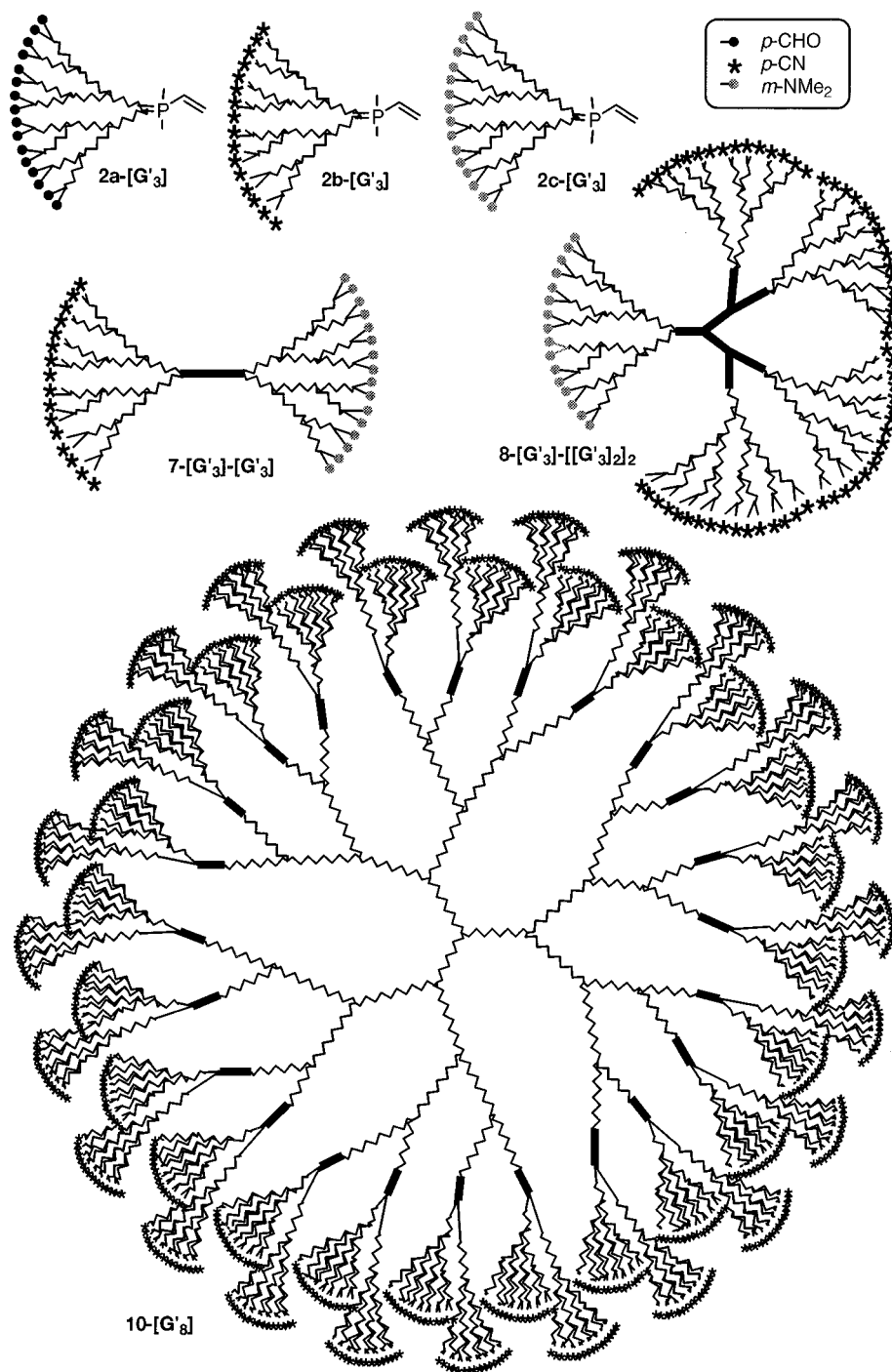


Figure 5. Schematized drawing of dendrons and dendrimers.

the signals corresponding to the $\text{CH}_2=\text{CH}-\text{P}=\text{N}-\text{P}=\text{S}$ linkage are easily detected by multinuclear NMR (the CH part is difficult to detect for the highest generations, due to the coupling with both phosphorus atoms). Thus, we decided to stop the growing of the dendron at this step, the third generation, to monitor readily the reactions we intended to do at the level of the core. Indeed, dendron **2a**-[G_3] can be easily functionalized on the surface or at the core; dendron **2a**-[G_3] is the elemental brick which will serve to build all of the multidendritic assemblies described in this paper.

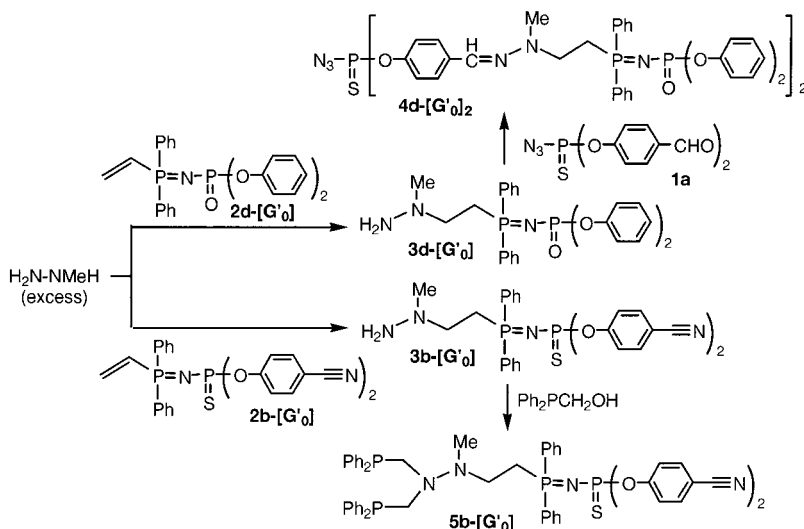
The easiest way to graft other functions on the surface of **2a**-[G_n] consists of reacting sodium salts of functionalized phenols such as 4-cyanophenol or 3-dimethylaminophenol instead of hydroxybenzaldehyde. These reactions have been carried out with the second and third generation dendrons,

leading to dendrons **2b**-[G'_2], **2b**-[G'_3], **2c**-[G'_2], and **2c**-[G'_3], respectively (Scheme 1, Figure 5).

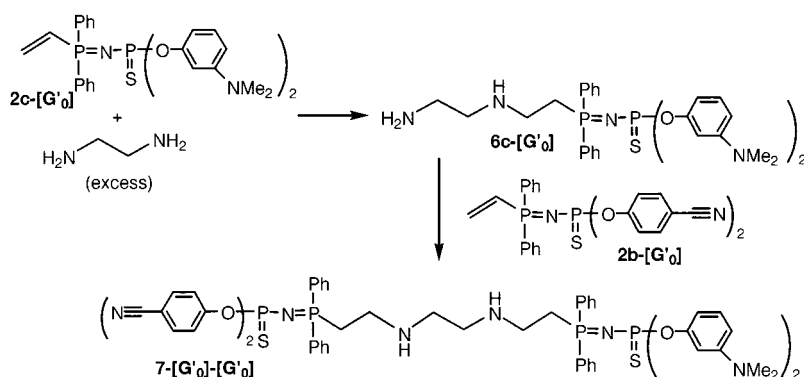
The Michael additions we intended to perform to graft new functions at the level of the core should present some difficulties; thus, we decided first to test these reactions on small models, easily synthesized and characterized, namely, compounds **2**-[G'_0]. Thermal additions of primary and secondary amines on vinylphosphine oxides generally occurs in very good yield, due to the activation of the double bond by the electron-withdrawing P=O group.²² Compound **2d**-[G'_0] possesses a P=N-P=O group which should be more electron-withdrawing than simple P=O groups, thus enhancing the reactivity of the vinyl group. Indeed, addition of 200% excess of methylhydra-

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Scheme 2



Scheme 3



zine on **2d-[G'₀]** at room temperature induces the formation of a single product, **3d-[G'₀]** (Scheme 2), as indicated in ^{31}P NMR by the deshielding of the signal corresponding to Ph_2PN ($\delta = 9.8$ for **2d-[G'₀]**, $\delta = 16.8$ for **3d-[G'₀]**). The reaction of the vinyl group is corroborated by the disappearance of the signals corresponding to $\text{CH}=\text{CH}_2$ in ^1H and ^{13}C NMR. Since methylhydrazine possesses one primary and one secondary amino group, the addition reaction might occur with either of these groups, the reaction with both groups being excluded by the presence of a single product in ^{31}P NMR. In fact, the reactive group is NMeH , as demonstrated later by the condensation of **3d-[G'₀]** with aldehydes. The same type of reaction, applied to compound **2b-[G'₀]** leads to **3b-[G'₀]**; in this case, the electron-withdrawing group is the $\text{P}=\text{N}-\text{P}=\text{S}$ linkage (Scheme 2). The addition induces the deshielding of the doublet corresponding to the $\text{Ph}_2\text{P}=\text{N}$ group in ^{31}P NMR from $\delta = 12.9$ for **2b-[G'₀]** to $\delta = 19.9$ for **3b-[G'₀]**. A spectacular shielding is also observed for the $\text{CH}_2=\text{CH}-\text{P}$ part in ^{13}C NMR, from 137.1 and 127.2 ppm, respectively for compound **2b-[G'₀]** to 54.1 and 25.0 ppm, respectively, for the $\text{CH}_2\text{CH}_2\text{P}$ part of compound **3b-[G'₀]**.

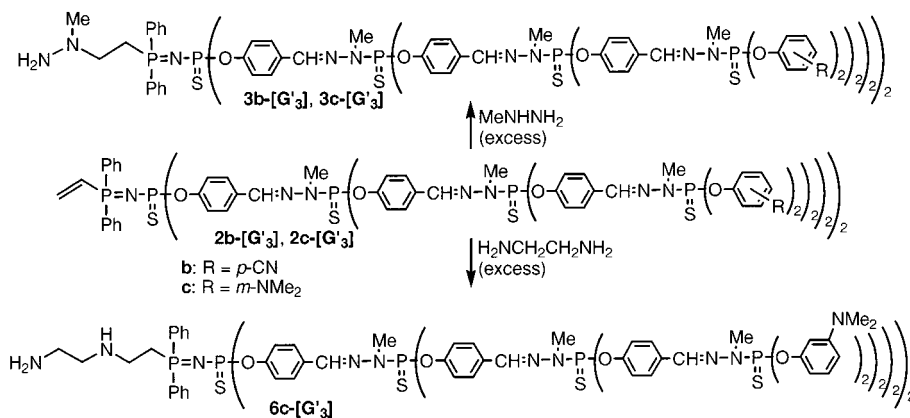
Thus, the Michael addition allows the grafting of primary amino groups which should be used later. Indeed, two equivalents of **3d-[G'₀]** undergo a Schiff condensation with both aldehyde groups of the phosphorus azide **1a**, indicating that **3d-[G'₀]** possesses one NH_2 group, and not two NH groups. This reaction leads to the formation of a new type of dendron, having an azido group at the core, **4d-[G'₀]₂** (Scheme 2). Besides the disappearance of signals corresponding to CHO and NH_2 in NMR and IR spectroscopies, an important shielding of the signal

of the CH_3 group is observed in ^{13}C NMR, from $\delta = 50.5$ for **3d-[G'₀]** to $\delta = 37.7$ for **4d-[G'₀]₂**.

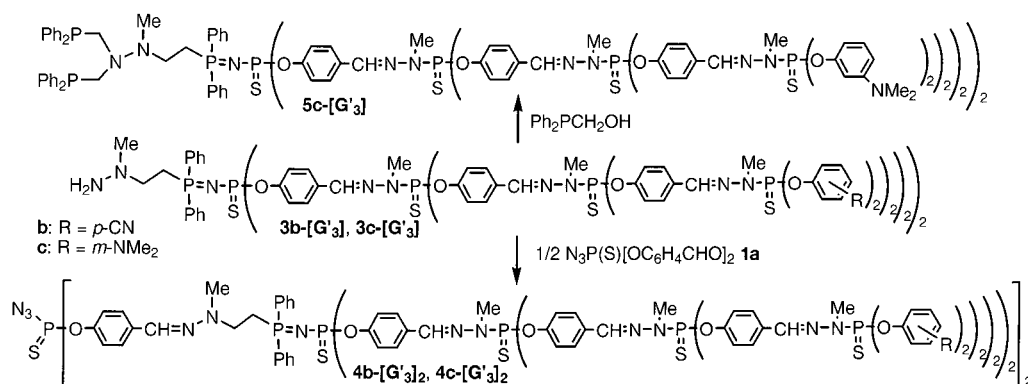
The NH_2 group of compound **3b-[G'₀]** undergoes another type of condensation reaction with two equivalents of $\text{Ph}_2\text{PCH}_2\text{OH}$ at 90°C . This reaction leads to the formation of a diphosphino group (Scheme 2), in a way that we have already experienced on the surface of dendrimers.^{18d,f} Compound **5b-[G'₀]** displays one singlet at $\delta = -23.8$, corresponding to the phosphino groups, besides the doublets corresponding to the $\text{P}=\text{N}-\text{P}=\text{S}$ linkage, in ^{31}P NMR. The occurrence of only one singlet for the $\text{Ph}_2\text{PCH}_2\text{N}$ group in ^{31}P NMR and only one doublet in ^{13}C NMR confirms the presence of one NH_2 group in compound **3b-[G'₀]**. Indeed, the presence of two nonequivalent NH groups would lead to a $\text{Ph}_2\text{PCH}_2\text{NMeNCH}_2\text{PPh}_2$ linkage which would display two singlets in ^{31}P NMR and two doublets for the CH_2 groups in ^{13}C NMR. A large shielding for the signal of the CH_3 group is also observed in ^{13}C NMR from $\delta = 50.6$ for **3b-[G'₀]** to $\delta = 33.6$ for **5b-[G'₀]**.

The Michael addition on the vinyl group can be applied to several types of primary and secondary amines, for instance, to ethylenediamine. The addition of a very large excess (32 000%) of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ to compound **2c-[G'₀]** at room temperature leads cleanly to compound **6c-[G'₀]** in a 1:1 reaction (Scheme 3). This compound possesses a primary and a secondary amino groups, which should react in their turn in a Michael addition. This assumption is demonstrated when **6c-[G'₀]** (170% excess) and **2b-[G'₀]** are reacted together at 90°C . ^{31}P NMR indicates that the reaction occurs to yield **7-[G'₀]-[G'₀]**, possessing two different types of end groups (Scheme 3). Indeed, the presence of two sets of two doublets corresponding to both types of $\text{P}=\text{N}$

Scheme 4



Scheme 5



N–P=S linkages, at $\delta = 16.2$ (Ph₂P) and 52.0 (P=S), both issued from the **6c-[G'₀]** part, and at $\delta = 19.5$ (Ph₂P) and 51.1 (P=S), both issued from the **2b-[G'₀]** part of **7-[G'₀]-[G'₀]** are detected.

In this case also, the question which arises concerns the amino group which reacts: is it the NH or the NH₂ group of **6c-[G'₀]**? A careful comparison between the ¹³C NMR spectra of **6c-[G'₀]** and **7-[G'₀]-[G'₀]** shows that among the signals corresponding to the H₂NCH₂CH₂NHCH₂CH₂P moieties, the first one (underlined) is the most modified by the reaction ($\Delta\delta = +10$ ppm for the first one, $\Delta\delta = -0.6$ ppm for the second one, respectively). This observation strongly suggests that the reaction occurred on the primary amino group and not on the secondary amino group of **6c-[G'₀]**. This result seems to be in contradiction with the reaction of methylhydrazine on compounds **2b,d-[G'₀]**, which occurs on the NH group, and with the known tendency of secondary amino groups to undergo Michael additions more easily than the primary one.²² However, the fact that the vinyl group of **2b-[G'₀]** is sterically hindered by both phenyl groups must be taken into account (see the X-ray structure of the related compound **2c-[G'₀]**, Figure 3). Thus, the NH group of **6c-[G'₀]** is itself too hindered to react with the vinyl group, whereas the NH₂ group located at the end of a spacer is non-hindered and does react, leading to **7-[G'₀]-[G'₀]**.

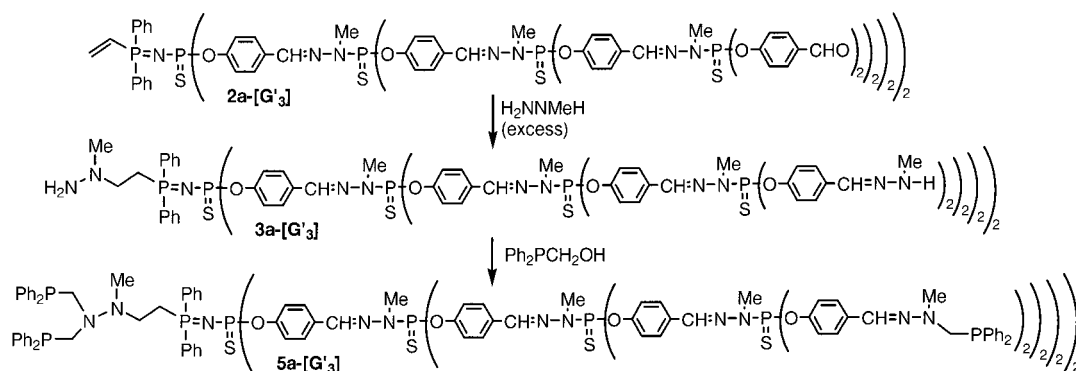
Having in hand several ways to functionalize the core and to associate these cores, we decided to apply these reactions to the third generation dendrons **2a-[G'₃]**, **2b-[G'₃]**, and **2c-[G'₃]**. Both dendrons **2b-[G'₃]** and **2c-[G'₃]** react with an excess of methylhydrazine (200% excess), leading cleanly to the formation of dendrons **3b-[G'₃]** and **3c-[G'₃]**, respectively (Scheme 4). In NMR spectra these compounds display characteristic signals for the R–CH₂CH₂P=N–P=S linkages the same as those found for the model compound **3b-[G'₀]**, in particular the deshielding

of the signal of the P=N group (from $\delta \sim 10$ to ~ 18 ppm) in ³¹P NMR, and the large shielding of the signal of the CH₂ group β to phosphorus (from $\delta \sim 137$ to ~ 54 ppm) in ¹³C NMR. A similar trend is observed for the reaction of a very large excess of ethylenediamine (40 000% excess) with **2c-[G'₃]**, leading to **6c-[G'₃]** (Scheme 4). These data indicate that the steric hindrance at the level of the core of the third generation dendrons is not more important than for the model compound. This fact is due to the great length of the branches (9.8 Å between P2 and P3 or P4 in compound **2a-[G'₁]**) and could be anticipated in view of the easy reactivity of the internal layers of dendrimers having the same type of branches.¹⁶ Thus, further reactions can be envisaged on the NH₂ group.

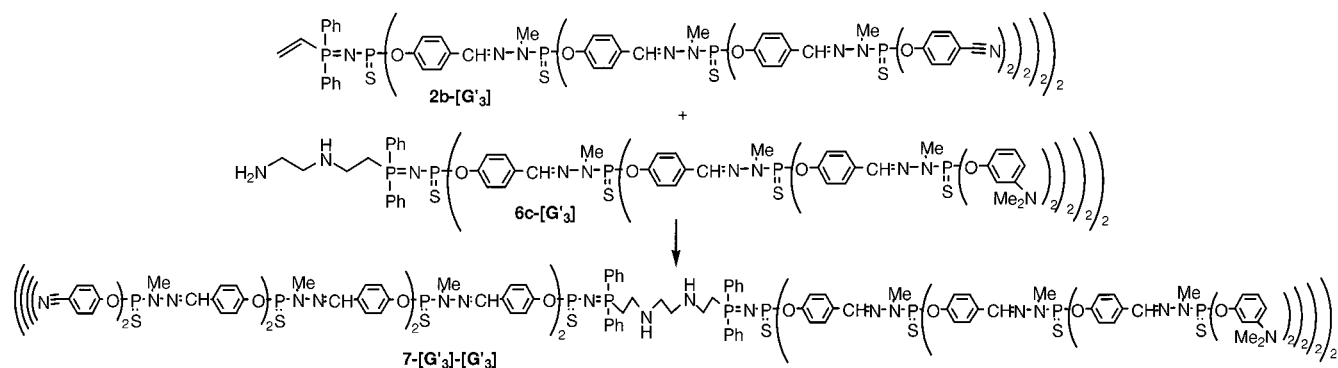
Two types of condensation reactions have been carried out from **3b-[G'₃]** and **3c-[G'₃]** (Scheme 5). The condensation of Ph₂PCH₂OH with the NH₂ group of dendron **3c-[G'₃]** at 90 °C leads to the formation of a diphosphino linkage at the core of dendron **5c-[G'₃]**. The most characteristic data of this compound is a singlet in ³¹P NMR at $\delta = -23.9$ for the tricoordinated phosphorus atoms, and a singlet in ¹³C NMR at $\delta = 52.8$ for the NCH₂PPh₂ group; these values correspond perfectly to those found for the model compound **5b-[G'₀]**.

The Schiff condensation of two equivalents of **3b-[G'₃]** or **3c-[G'₃]** with both aldehyde groups of the phosphorus azide **1a** induces the association of two dendrons, leading to **4b-[G'₃]₂** or **4c-[G'₃]₂**, respectively. The condensation induces in ¹³C NMR the large shielding of the CH₃ group of the core (from ~ 50.5 ppm for **3b-c-[G'₃]** to ~ 37.8 ppm for **4b-c-[G'₃]₂**) already observed for the **3d-[G'₀]** → **4d-[G'₀]₂** transformation. Compounds **4b-[G'₃]₂** and **4c-[G'₃]₂** possess an azido group at the core and can be viewed as fourth generation layered dendrons made up of two types of layers: one having S=POC₆H₄CH=

Scheme 6



Scheme 7



NNMeCH₂CH₂PPh₂=N linkages, the other one having S=POC₆H₄CH=NNMe linkages repeated three times (Scheme 5).

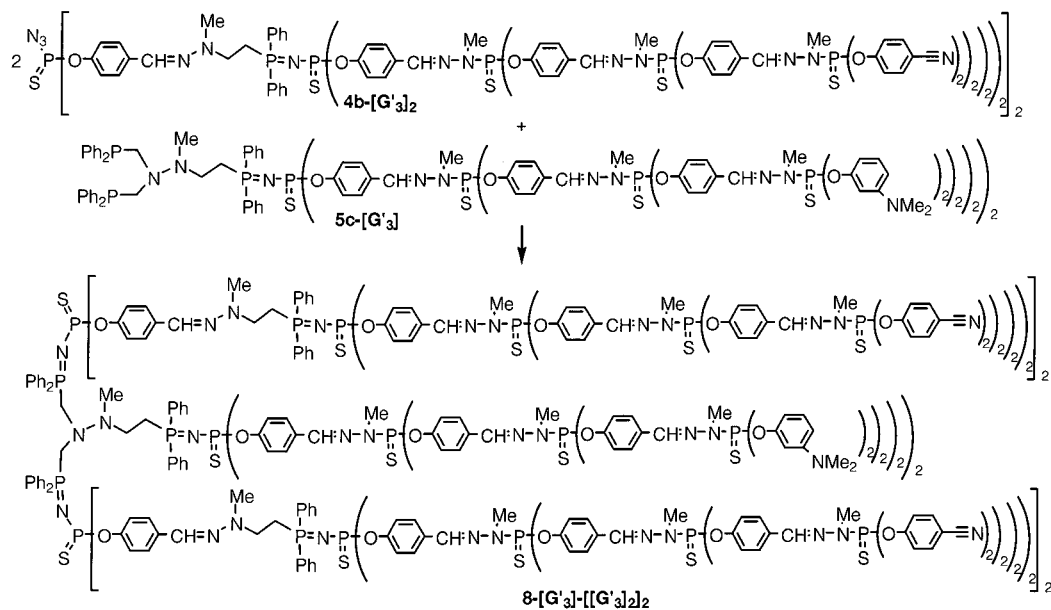
The third generation dendron **2a**-[G'₃] is expected to behave in a very special way when reacted with methylhydrazine. Indeed, this compound possesses both one vinyl group able to undergo the addition of the NHMe part of methylhydrazine, and 16 aldehyde groups able to undergo the condensation with the NH₂ part. To prevent the reaction of some methylhydrazine molecules on both sides, an excess (200%) is used (Scheme 6). The formation of dendron **3a**-[G'₃] induces the disappearance of signals corresponding to both CH₂=CH and CHO groups in ¹H NMR, indicating that both addition and condensation occurred. Of course, it is not possible to ascertain in this case that the same molecule of methylhydrazine did not react on both sides. However, if this type of reaction occurred, it is only as a marginal process. Indeed, the ¹³C NMR spectra of **3a**-[G'₃] compared to those of **2a**-[G'₃] indicate the appearance of only two new signals for the CH₃ groups at δ = 34.6 (CH₃NHN=CH) and 50.4 (H₂NNCH₃CH₂CH₂P); the formation of PCH₂CH₂NCH₃N=CH linkages should give an additional signal presumably at ~38 ppm (see ¹³C NMR spectra of compounds **4**-[G'₃]₂), which is not observed. The use of Ph₂PCH₂OH on **3a**-[G'₃] allows the grafting of monophosphino groups on the surface and of a diphosphino group at the core. Both types of groups give slightly different signals in ³¹P NMR (δ = -23.5 for NMeCH₂PPh₂ and -23.9 for N(CH₂PPh₂)₂) besides the signals corresponding to the skeleton of dendron **5a**-[G'₃] (Scheme 6).

These experiments give dendrons possessing either a vinyl, a primary amino, a diphosphino, or an azido group at the level of the core. All of these compounds are useful precursors of multidendritic systems. For instance, a Michael addition between dendron **6c**-[G'₃] (100% excess) and dendron **2b**-[G'₃] at 90 °C induces the formation of dendrimer **7**-[G'₃]-[G'₃] (Scheme 7). This compound is purified from the excess of **6c**-[G'₃] by

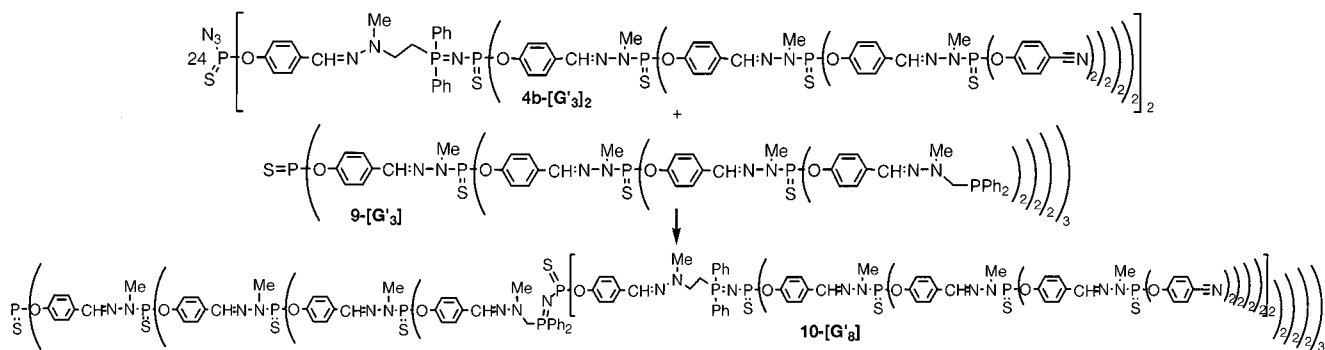
size-exclusion chromatography. The NMR data concerning the core of **7**-[G'₃]-[G'₃] are different from those of **7**-[G'₀]-[G'₀]. Indeed, in the later compound, the surface is close to the core; thus, the presence of two types of functions on the surface induces a dissymmetry of all of the components of the (S)PN=PPh₂CH₂CH₂NHCH₂CH₂NHCH₂CH₂PPh₂=NP(S) linkage, which gives distinct signals for all the atoms. In contrast, the surface of **7**-[G'₃]-[G'₃] is far from the core; thus, the dissymmetry of the surface has no influence upon the core, which is symmetrical. In this case, both P=N-P=S linkages give only two doublets in ³¹P NMR at δ = 17.3 and 52.0, both PCH₂CH₂NH linkages give only one doublet and one singlet in ¹³C NMR at δ = 27.8 and 41.3, respectively, and the NHCH₂CH₂NH linkage gives only one singlet at δ = 52. Compound **7**-[G'₃]-[G'₃] is a surface-block dendrimer; indeed, even if the internal skeleton is identical on both sides, this dendrimer possesses two different faces: 16 dimethylamino groups on one side, 16 nitrile groups on the other side (Figure 5).

Another type of surface-block dendrimer is obtained when two equivalents of dendron **4b**-[G'₃]₂, having an azide at the core, are associated with one equivalent of dendron **5c**-[G'₃], having two phosphino groups at the core, via two Staudinger reactions (Scheme 8). The formation of dendrimer **8**-[G'₃]-[[G'₃]₂]₂ is characterized by the disappearance of the singlets corresponding to the tricoordinated phosphorus atoms (δ³¹P = -23.9 for **5c**-[G'₃]) and the N₃P groups (δ³¹P = 59.8 for **4b**-[G'₃]₂). The Ph₂P=N-P=S linkages formed by these associations are distinguishable from the other Ph₂P=N-P=S linkages, particularly the Ph₂P groups which give a doublet at δ = 13.9 for the NCH₂Ph₂P groups which reacted and another doublet at δ = 18.0 for the NCH₂CH₂PPh₂ groups. Furthermore, the shielding of the signal of the carbon atom α to the tricoordinated phosphorus atom which undergoes the reaction from δ¹³C = 52.8 for **5c**-[G'₃] to δ¹³C = 50.0 for **8**-[G'₃]-[[G'₃]₂]₂, and the modification of the shape of this signal (singlet for **5c**-[G'₃],

Scheme 8



Scheme 9



doublet with $^1J_{\text{CP}} = 80$ Hz for **8-[G'3]-[[G'3]2]2**) are characteristic of a change in the coordination of phosphorus and thus confirm that the Staudinger reaction occurred. **8-[G'3]-[[G'3]2]2** is both a surface-block and a layer-block dendrimer. Indeed, on one hand the internal layers close to the core possess P=N-P=S linkages, whereas the other internal layers have not, and on the other hand two types of end groups are located in definite areas of the surface in a 1/4 ratio (16 dimethylamino groups and 64 nitrile groups) (Figure 5).

Dendron **4b-[G'3]2** having an azide at the core can also be used to multiply rapidly the number of end groups of a dendrimer possessing phosphino groups at the surface. Indeed, the reaction of 24 equivalents of **4b-[G'3]2** with one equivalent of the third generation dendrimer **9-[G'3]** possessing 24 diphenylphosphino end groups^{18e} leads in one step to the formation of the eighth generation dendrimer **10-[G'8]** possessing 768 nitrile end groups (Scheme 9). The formation of dendrimer **10-[G'8]** is characterized by the disappearance of the singlets corresponding to the N_3P groups of **4b-[G'3]2** and the PPh_2 groups of **9-[G'3]** in ^{31}P NMR, and by the appearance of a doublet characteristic of the $\text{NCH}_2\text{Ph}_2\text{PN}$ group at $\delta = 13.9$. Signals very characteristic of the $\text{CH}_3\text{NCH}_2\text{PPh}_2=\text{N}-\text{P}=\text{S}$ linkages also appear in ^{13}C NMR. Indeed, this linkage give signals different from those obtained for the $\text{CH}_3\text{NCH}_2\text{PPh}_2$ part of **9-[G'3]** and also different from those obtained for the $\text{CH}_3\text{-NCH}_2\text{CH}_2\text{PPh}_2=\text{N}-\text{P}=\text{S}$ linkages also included in the skeleton of **10-[G'8]**. The most characteristic signals concern the CH_2

groups α to phosphorus, located at $\delta = 25.0$ ($^1J_{\text{CP}} = 65$ Hz) for the $\text{CH}_2\text{-CH}_2\text{PPh}_2$ groups of **4b-[G'3]2** and **10-[G'8]**, $\delta = 60.9$ ($^1J_{\text{CP}} = 10$ Hz) for the NCH_2PPh_2 groups of **9-[G'3]**^{18e} and $\delta = 56.0$ ($^1J_{\text{CP}} = 80$ Hz) for the NCH_2PPh_2 groups of **10-[G'8]**. Thus, in this case also, the Staudinger reaction induces important changes in the ^{13}C chemical shifts and coupling constants for the CH_2 groups α to phosphorus. Compound **10-[G'8]** is a layer-block dendrimer (Figure 5), possessing $\text{NCH}_2\text{PPh}_2=\text{N}-\text{P}=\text{S}$ linkages at the level of the fourth generation and $\text{NCH}_2\text{CH}_2\text{-PPh}_2=\text{N}-\text{P}=\text{S}$ linkages at the level of the fifth generation, both linkages being absent in the skeleton of the other generations.

The previous examples show that dendrons **4-[G'3]2** possessing an azide at the core can be grafted to the core of another dendron or to the surface of a dendrimer, provided they bear phosphino groups. Having in hands dendron **5a-[G'3]** which have phosphino groups both at the level of the core and on the surface, we decided to react it with dendron **4c-[G'3]2** (Scheme 10). The Staudinger reaction occurs both at the level of the core and on the surface of **5a-[G'3]**, leading to the "unsymmetrical" dendrimer **11-[G'4]2-[G'8]** possessing 576 dimethylamino groups on the surface (Figure 6). The reaction is monitored by ^{31}P NMR, which shows the total disappearance of signals corresponding to N_3P and to tricoordinated phosphorus atoms, and the appearance of a doublet corresponding to the $\text{NCH}_2\text{Ph}_2\text{PN}$ linkages at $\delta = 13.9$. The occurrence of the Staudinger reaction both at the level of the core and on the surface of **5a-[G'3]** is confirmed by ^{13}C NMR. Indeed, the signals corresponding to

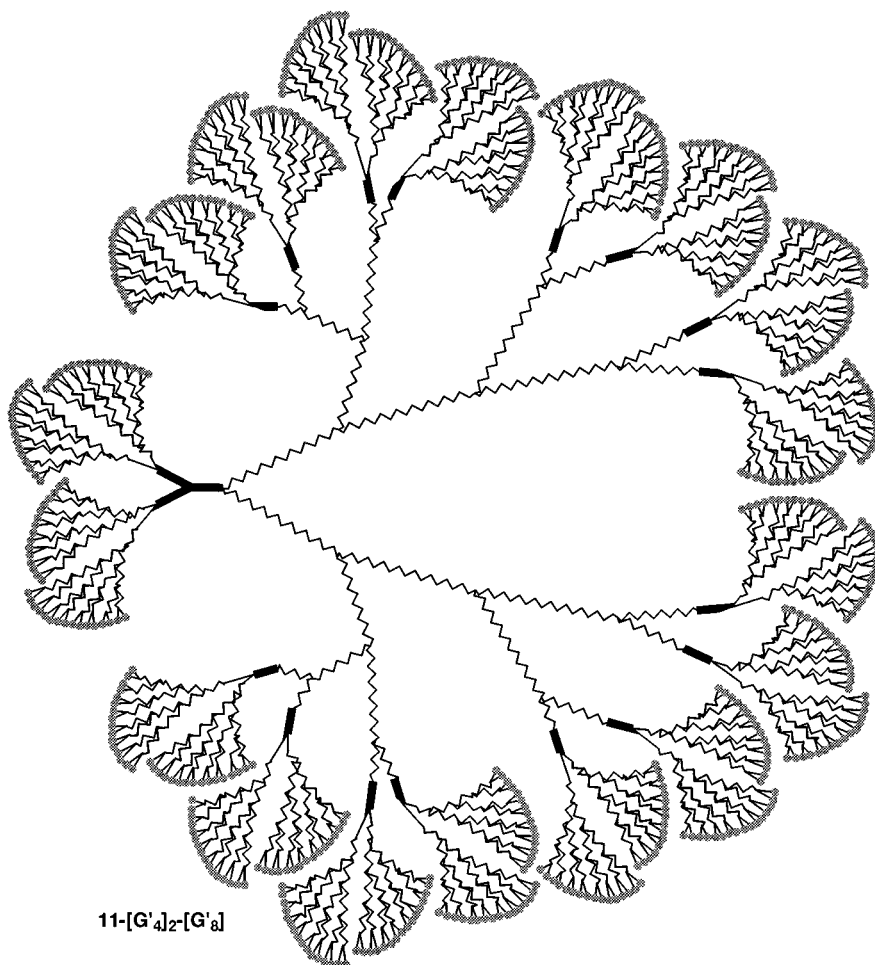
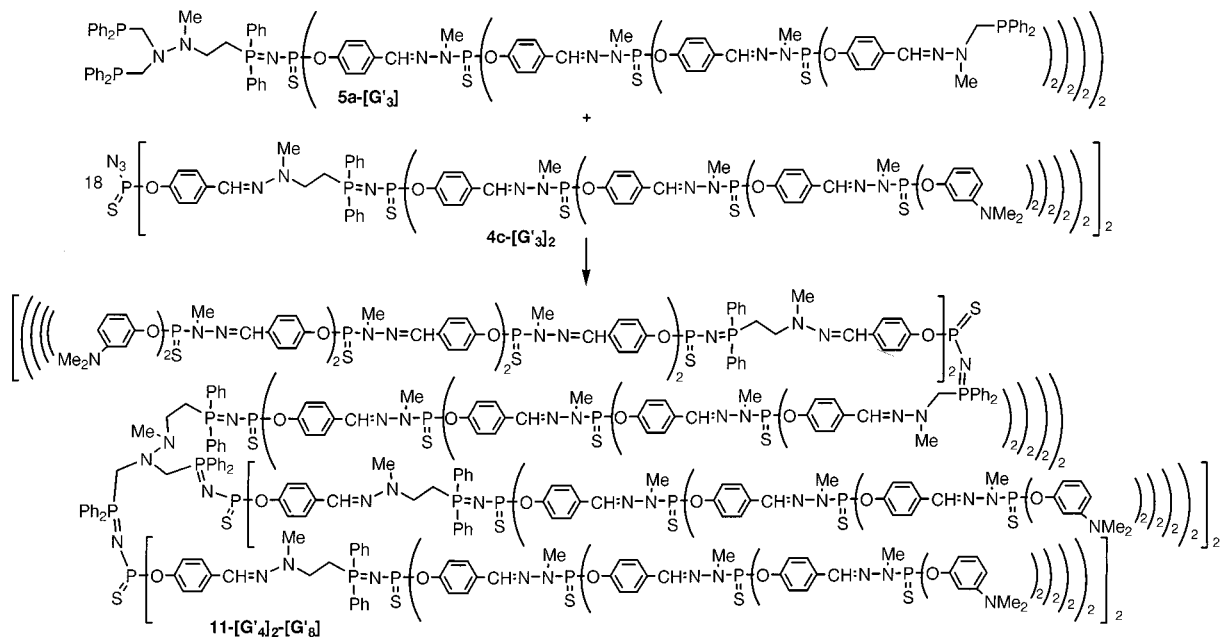


Figure 6. Schematized drawing of dendrimer **11-[G'4]2-[G'8]**.

Scheme 10



the CH₂ groups α to the tricoordinated phosphorus atoms undergo a shielding and an increase of the ¹J_{CP} coupling constant during the transformation **5a-[G'3]** → **11-[G'4]2-[G'8]** from δ = 53.5 (¹J_{CP} = 4 Hz) to δ = 51.8 (broad doublet, ¹J_{CP} ~80 Hz) for the NCH₂P groups of the core, and from δ = 60.9 (¹J_{CP} = 10.7 Hz) to δ = 56.0 (¹J_{CP} = 70 Hz) for the NCH₂P groups

of the surface. Compound **11-[G'4]2-[G'8]** is a kind of layered segment-block dendrimer having two fourth generation dendrons and one eighth generation layered dendron linked to a (PCH₂)₂-NNMeCH₂CH₂P trifunctional core (Figure 6).

Physical Properties. The molecular peak of dendrons is detected by MALDI TOF experiments. However, this technique

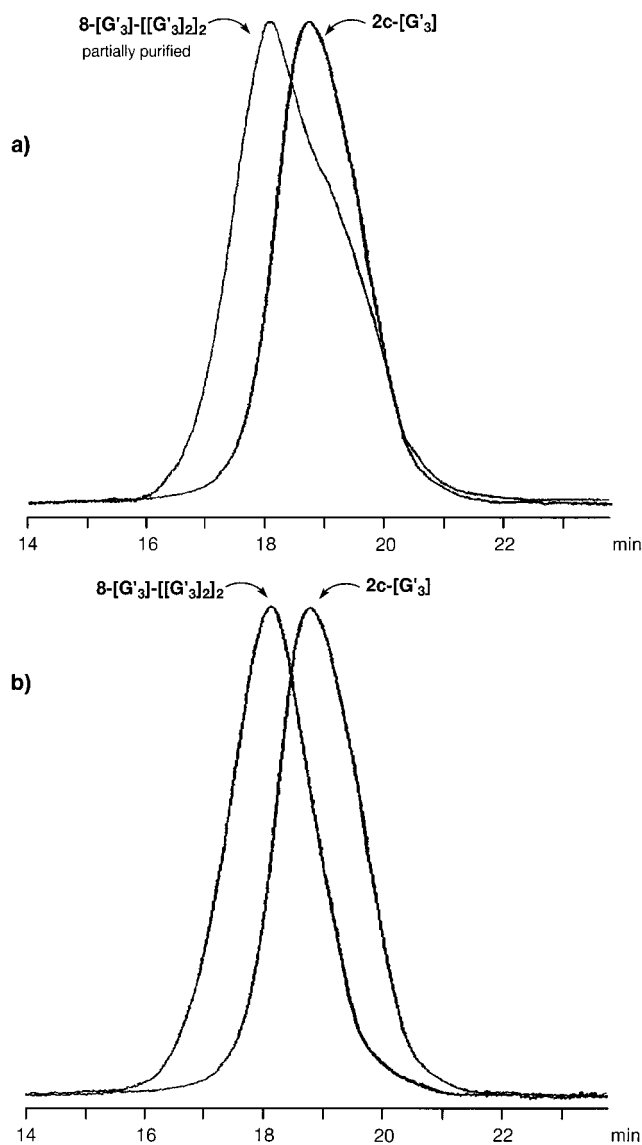


Figure 7. SEC traces of compounds $2c\text{-}[\text{G}'_3]$ and $8\text{-}[\text{G}'_3]\text{-}[[\text{G}'_3]_2]_2$.

appeared not useful for the detection of structure defects since the irradiation of these dendrimers at 350 nm provokes the cleavage of a number of bonds (hydrazino units) as shown by ^{31}P NMR.²³ Indeed, the UV spectra of these dendrimers show a very broad absorption at 210–360 nm, thus including the wavelength of the laser light used for MALDI TOF experiments (337 nm).

However, the degree of purity of dendrons and dendrimers can be checked by size-exclusion chromatography. Chromatograms of dendrons $2b\text{-}[\text{G}'_3]$ and $2c\text{-}[\text{G}'_3]$ indicate that their polydispersity is comparable to or better than that of narrow distribution polystyrene standards (polydispersity $M_w/M_n = 1.03$). The SEC trace for $2c\text{-}[\text{G}'_3]$ is depicted Figure 7. Comparison of the SEC trace of $8\text{-}[\text{G}'_3]\text{-}[[\text{G}'_3]_2]_2$ with that of dendron $2c\text{-}[\text{G}'_3]$ indicates that $8\text{-}[\text{G}'_3]\text{-}[[\text{G}'_3]_2]_2$ has a narrow molecular weight distribution (Figure 7). Furthermore, the elimination of the excess of dendron $2c\text{-}[\text{G}'_3]$ is easily monitored by SEC, as can be seen when comparing Figure 7a ($8\text{-}[\text{G}'_3]\text{-}[[\text{G}'_3]_2]_2$ partially purified, contaminated by traces of $2c\text{-}[\text{G}'_3]$) and Figure 7b ($8\text{-}[\text{G}'_3]\text{-}[[\text{G}'_3]_2]_2$ purified). The retention time of $8\text{-}[\text{G}'_3]\text{-}[[\text{G}'_3]_2]_2$ is smaller than that of the dendron, confirm-

ing the increase of the molecular weight. In fact, a plot of log molecular weight versus retention time for the dendrons and dendrimers described in this paper, including the very special dendrimer $11\text{-}[\text{G}'_4]_2\text{-}[\text{G}'_8]$, gives a relatively straight line (Figure 8). In the same conditions, polystyrene standards give another straight line, with a different slope which increasingly deviates from the dendrons and dendrimers plot as molecular weight increases. This tendency was already described³ and was attributed to the increase of the density and compactness of dendritic macromolecules as molecular weight increases.

However, it must be emphasized that the molecular weight is not the single parameter which influences the physicochemical properties of these dendritic macromolecules. Indeed, the differential scanning calorimetry experiments for dendrons $2b\text{-}[\text{G}'_3]$ and $2c\text{-}[\text{G}'_3]$, which differ only by the nature of the functional group linked to the surface, gives a drastic difference, as already reported for other dendrons;^{6c,15b} the T_g value is 377 K for $2b\text{-}[\text{G}'_3]$ (16 CN end groups) and 341 K for $2c\text{-}[\text{G}'_3]$ (16 NMe₂ end groups). It must be noted also that the dendrimers constituted of both $2b\text{-}[\text{G}'_3]$ and $2c\text{-}[\text{G}'_3]$ have only one T_g , with a value intermediate between the values found for these dendrons. The occurrence of only one T_g (and not two) in dendritic macromolecules containing blocks of different chain end substitution was already reported.^{13a,14b,15a} The T_g value for dendrimer $7\text{-}[\text{G}'_3]\text{-}[\text{G}'_3]$ is 357 K and that for $8\text{-}[\text{G}'_3]\text{-}[[\text{G}'_3]_2]_2$ is 352 K.

Conclusions

The presence of 16 chlorines on the surface and one vinyl group at the core of the third generation dendron $2a\text{-}[\text{G}_3]$ allows specific new functionalizations independently of the surface with functionalized phenols and of the core with various amines. These functionalizations finally induce the presence of primary amines, phosphines, or azide at the core. Such functions display a versatile reactivity, leading to the formation of an unprecedented series of dendritic macromolecules with very special architectures through core–core, core–surface, or core–core–surface–core couplings. Layer-block dendrons ($4b\text{-}[\text{G}'_3]_2$, $4c\text{-}[\text{G}'_3]_2$), a surface-block dendrimer ($7\text{-}[\text{G}'_3]\text{-}[\text{G}'_3]$), a layer-block dendrimer ($10\text{-}[\text{G}'_8]$), layered surface-block dendrimer ($8\text{-}[\text{G}'_3]\text{-}[[\text{G}'_3]_2]_2$), and segment-block dendrimer ($11\text{-}[\text{G}'_4]_2\text{-}[\text{G}'_8]$) have been obtained in this way. Two types of functional groups can be located in definite areas on the surface of several of these dendrimers. These functions may have complementary properties such as donor (NMe₂) and acceptor (C≡N) properties; obviously, this reactivity could be extended to the grafting of many other types of functions. It must be emphasized also that these very complex and varied macromolecules are obtained in a few steps from a common precursor, $2a\text{-}[\text{G}_3]$. Such an approach allows the very rapid multiplication of the number of end groups in one step, for instance from 24 to 768 for the $9\text{-}[\text{G}'_3] \rightarrow 10\text{-}[\text{G}'_8]$ transformation, or from 16 to 576 for the $5a\text{-}[\text{G}'_3] \rightarrow 11\text{-}[\text{G}'_4]_2\text{-}[\text{G}'_8]$ transformation. Work is underway to apply this approach to the synthesis of other types of dendritic architectures with specific properties, in particular, in the field of mixed organic–inorganic chemistry and material sciences.

Experimental Section

General. All manipulations were carried out with standard high-vacuum and dry-argon techniques. ^1H , ^{13}C , ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, or AMX 400 spectrometers. References for NMR chemical shifts are 85% H₃PO₄ for ^{31}P NMR, SiMe₄ for ^1H and ^{13}C NMR. The attribution of ^{13}C NMR signals has been done using J_{mod} , two-dimensional HMBC, and HMQC, broad

(23) Blais, J. C.; Turrin, C.; Caminade, A. M.; Majoral, J. P., to be published.

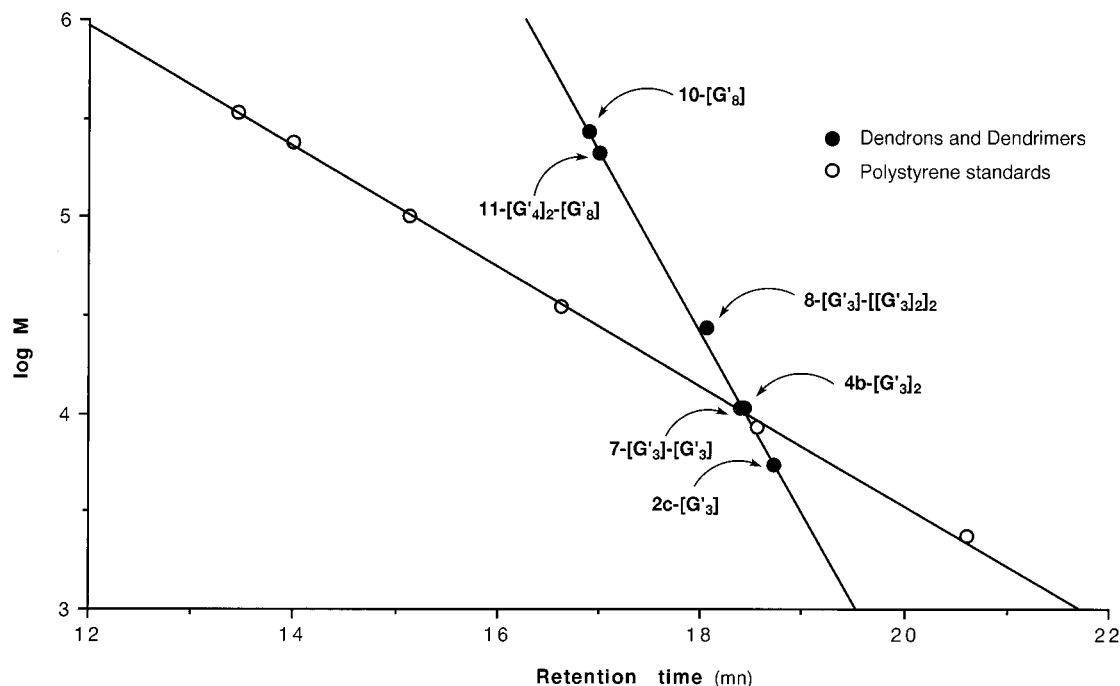


Figure 8. Plot of SEC retention time versus logarithm of molecular weight for polystyrene standards and dendrons and dendrimers.

Table 1. Crystallographic Data

	1b	2c-[G'0a] - 2c-[G'0b]	2a-[G1]
asymmetric unit	C ₁₄ H ₈ N ₅ PS	C ₆₀ H ₆₆ N ₆ O ₄ P ₄ S ₂	C ₃₀ H ₂₉ Cl ₄ N ₅ O ₂ P ₄ S ₃
molecular weight	341.28	1123.19	853.44
ρ_{calcd} (g·cm ⁻³)	1.433	1.294	1.466
μ (cm ⁻¹)	3.21	2.56	6.70
F_{000}	348	2368	876H
crystal system	triclinic	monoclinic	triclinic
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> (Å)	8.6198(15)	17.9530(17)	10.7742(15)
<i>b</i> (Å)	9.0671(16)	10.8093(10)	13.955(2)
<i>c</i> (Å)	11.284(2)	30.051(3)	14.805(2)
α (deg)	90.03(2)	90	107.250(16)
β (deg)	91.85(2)	98.657(11)	109.204(15)
γ (deg)	116.183(19)	90	98.361(17)
<i>V</i> (Å ³)	790.9(2)	5765.3(10)	1933.4(5)
<i>Z</i>	2	4	2
crystal size	0.3 × 0.2 × 0.04	0.25 × 0.07 × 0.05	0.2 × 0.1 × 0.1
crystal shape	thin plate	thin plate	parallelepiped
crystal color	colorless	colorless	colorless
<i>R</i>	0.0875	0.0608	0.0419
wR2	0.1051	0.1169	0.0969
G.O.F	1.134	1.009	1.024

band, or CW ³¹P decoupling experiments when necessary. DSC spectra were recorded with a NETZSCH DSC 204 machine. Compound **1a** was prepared according to a published procedure²⁴ Preparative size-exclusion chromatography was performed using Bio-Beads S-X1 beads (operating range 600–14000 g·mol⁻¹) from Bio-Rad company and THF as eluent. SEC analytical data were obtained at 37 °C using a Waters 410 differential refractometer, three 5 μm Waters Styragel HR columns (300 × 8 mm) connected in series in order of decreasing pore size (10 000 Å, 1000 Å, 100 Å) and THF as eluent with a nominal flow of 1.2 mL/min.

General Procedure for the Synthesis of 2a-d-[G'_n]. To a solution of diphenylvinylphosphine (typically 5 mmol) in CH₂Cl₂ (typically 10 mL) was added at 0 °C one equivalent of **1a-d**. Ten minutes after the end of the addition, the mixture was warmed to room temperature and stirred for 3 h, and then the solvent was removed under vacuum.

General Procedure for the Synthesis of 2a-[G'_n] (n = 1–3). To a solution of **2a-G'_{n-1}** (typically 2 g) in THF (typically 20 mL) was

added a small excess of dichloromethylhydrazinothiophosphine in solution in chloroform. The mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the product was washed several times with a mixture THF/pentane (1/5) to give **2a-[G'_n] (n = 1–3)** as white powders. Single crystals of **2a-[G₁]** suitable for X-ray diffraction were grown in a THF/pentane (1/5) solution at room temperature.

General Procedure for the Synthesis of 2a-c-[G'_n] (n = 1–3). To a solution of **2a-[G'_n]** (typically 2 g) in THF (typically 20 mL) was added a small excess of sodium salt **1a**, **1b**, or **1c**. The resulting mixture was stirred at room temperature for 12 h. The solution was first centrifuged and then evaporated under vacuum. The product was washed with a mixture THF/pentane (1/5) to give a white powder for **2a-[G'_n]** and **2b-[G'_n]** or a brown powder for **2c-[G'_n]**.

X-ray Analysis of Compounds 1b, [2c-[G'_{0a}], 2c-[G'_{0b}], and 2a-[G₁]. Data collection was performed at low temperature (*T* = 160 K) for three compounds on a STOE imaging plate diffraction system (IPDS), equipped with an Oxford Cryosystems Cryostream cooler device and using a graphite monochromatized Mo K α radiation (λ =

(24) Mitjaville, J.; Caminade, A. M.; Mathieu, R.; Majoral, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 5007.

0.71073 Å). The crystal-to-detector distance was chosen to be 80 mm, owing to a low diffraction density at an angle of Bragg higher than 24°. Final unit cell parameters for each measurement were obtained by a least-squares refinement on a set of 5000 reflections equally distributed in reciprocal space, and a crystal decay was monitored by measuring 200 reflections per image. Any fluctuations of the intensity were observed over the course on the data collection.

The structures were solved by direct methods using (SIR92)²⁵ and refined by least-squares procedures on F^2 with the aid of (SHELXL-97)²⁶ by minimizing the function: $\sum w(F_o^2 - F_c^2)^2$, where F_o and F_c are respectively the observed and calculated structure factors. The atomic scattering factors were taken from *International Tables for X-ray Crystallography*.²⁷ All hydrogen atoms have been located on difference Fourier maps for whole structures but introduced in a process of calculation in a riding model with isotropical thermal parameters fixed at 20% higher than those of the carbon atoms to which they were connected. All non-hydrogen atoms were anisotropically refined, a statistical disorder having been found for one *N*-dichlorothiophosphoranyl group of compound **2a**-[**G**₁]. Chlorine and sulfur atoms of this group have been anisotropically refined on two positions with an

(25) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *SIR92*; program for automatic solution of crystal structures by direct methods. *J. Appl. Cryst.* **1994**, *27*, 435.

(26) Sheldrick, G. M.; *SHELXL97*; program for the refinement of crystal structures; University of Göttingen: Germany, 1997.

(27) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

occupancy found to be close to 0.5. A weighting scheme was used in the last cycles of refinement, where weights are calculated from the following formula: $\text{weight} = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Molecules are illustrated using the program ZORTEP²⁸ with a 50% probability displacement ellipsoids for non-hydrogen atoms. Main data concerning the crystals and the X-ray analysis are gathered in Table 1.

Further details concerning the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge, UK.

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Supporting Information Available: Experimental procedures and characterization data for new compounds. ZORTEP drawing and Tables of crystal data, data collection, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1b**, [**2c**-[**G**'_{0a}], **2c**-[**G**'_{0b}]] and **2a**-[**G**₁] (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(28) Zolnai, L. *ZORTEP*; graphical Program for X-ray structures analysis; University of Heidelberg: Germany, 1998.