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Phosphine-terminated dendrimers Synthesis and complexation properties

Anne-Marie Caminade[1], Régis Laurent, Bruno Chaudret, Jean Pierre Majoral *

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse, Cedex 4, France

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Contents

Abstract

Several ways of synthesis of phosphine-terminated dendrimers are described. The diphenylphosphine group, which is used in almost all cases, can be either a component of the reiterative process of synthesis of the dendrimer or can be grafted only on the surface, after the synthesis of the dendrimer. The PPh_2 moieties are linked to various types of surface groups, including chiral substituents. In one case, the synthesis has been carried out to the tenth generation (3072 PPh_2 end groups). The complexation properties of the phosphine and diphosphine-terminated dendrimers have been studied toward various transition metal derivatives, including W, Fe, Ru, Rh, Pd, Pt, and Au.

Keywords: Dendrimer; Phosphine; Complexation

* Corresponding author. Fax: +33 5 61 55 30 03; e-mail: majoral@lcc-toulouse.fr
[1] Also corresponding author

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1. Introduction

The exponential growth of the work devoted to the coordination chemistry of phosphorus over more than 50 years was in fact restricted to topologically simple phosphines until the mid-1970s. Then, the behavior of more sophisticated ligands such as phosphorus-containing macrocycles [1] and phosphorus-containing cryptands [1,2] was investigated. The recent development of a new class of macromolecules with a special topology, namely dendrimers (for reviews on dendrimers, see for example refs. [3–11]), should have promoted a versatile coordination chemistry. Indeed, their highly branched structure (Fig. 1), which induces the location of all the reactive functions on the surface, has already been used to complex various transition metals (see for example refs. [12–19]). These dendrimeric complexes exhibit interesting properties in several fields such as catalysis [14] or molecular recognition of anions [18]. However, in most cases, the ligating sites are either cyclopentadiene groups or nitrogen, and very few phosphine-terminated dendrimers have been used so far as ligands. The first report concerned palladium complexes [up to five (P)Pd($NCCH_3$) groups] of the first and second generation of dendrimers built with phosphine groups at all the junctions; they were used to catalyze the electrochemical reduction of CO_2 to CO [20,21]. Another report concerned the complexation of gold by diphenylphosphine groups grafted on the periphery of polyamine dendrimers, to generation four (up to 32 $Ph_2P{\rightarrow}Au{-}Cl$ groups) [22,23].

We have described the synthesis of several types of phosphine-terminated dendrimers, as well as their complexes with Group 6, 8, 9, 10, and 11 metals. This paper is an account of this work.

2. Synthesis of phosphine-terminated dendrimers

As seen above, the phosphine groups can be introduced either during the reiterative process of synthesis of the dendrimer, or grafted on the surface after the synthesis of the dendrimer. We have carried out both types of experiments; in all cases,

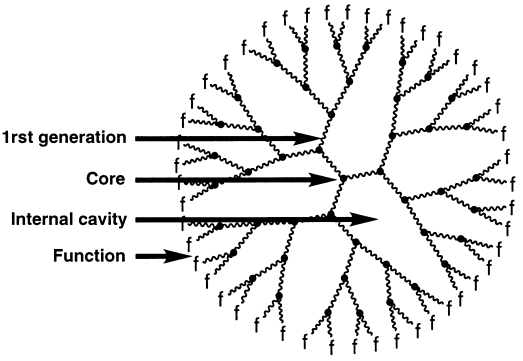


Fig. 1. Fourth generation of a dendrimer.

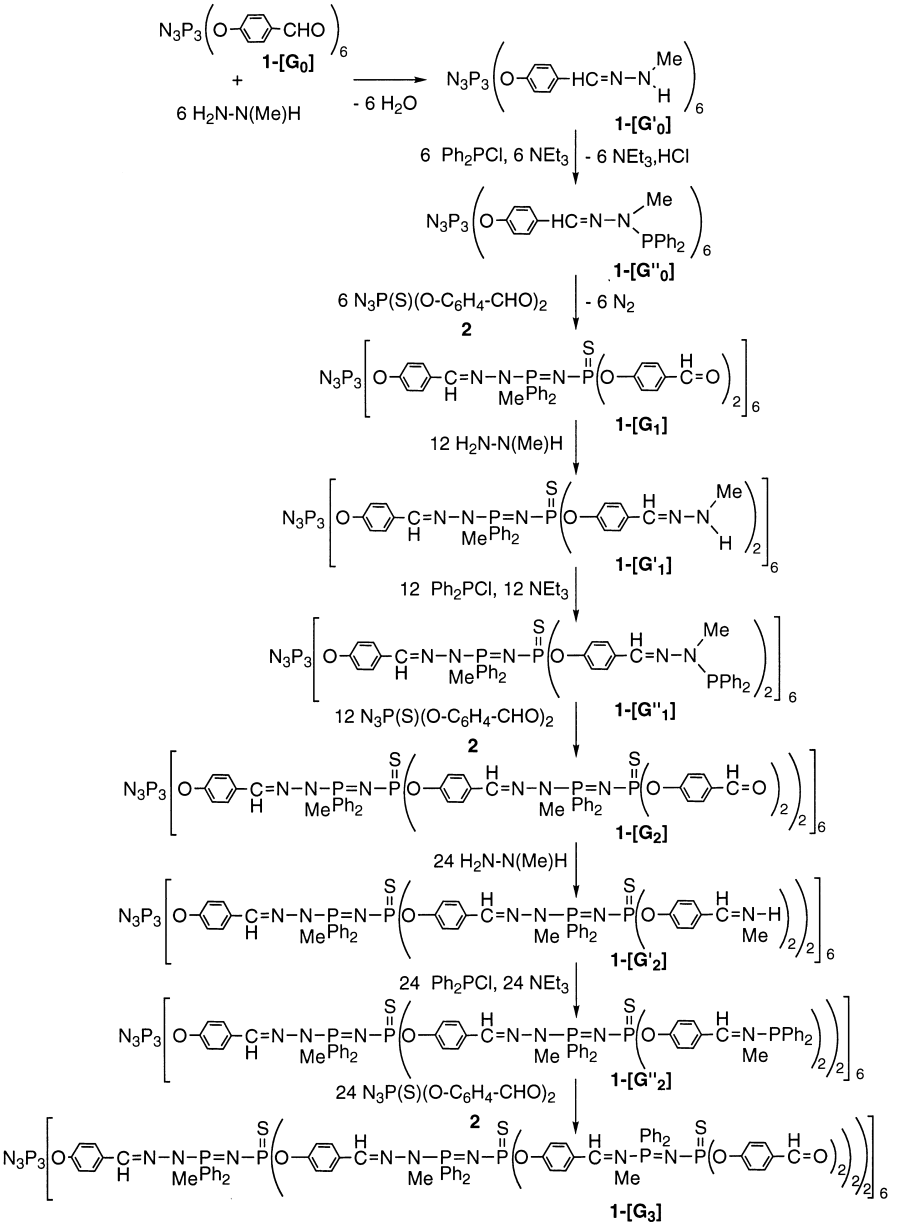
reactions are monitored by ^{31}P NMR, which appears to be a unique and indispensable tool to characterize these giant molecules.

2.1. Phosphine groups as components of the reiterative process of synthesis

We have described several types of synthesis which imply the use of tricoordinated phosphorus derivatives to synthesize very small dendrimers, generally only to the first generation [24,25]. However, we have discovered a more convenient method, which provides dendrimers to the third generation (24 or 48 end groups, depending on the number of functions of the core) [26]. The reiterative process consists of three steps: (i) a Schiff reaction, (ii) a substitution reaction, and (iii) a Staudinger reaction which allows us to double the number of terminal functions. The starting reagent (the core) must bear several aldehyde functions. We have carried out experiments starting either from the hexaaldehyde $N_3P_3(O–C_6H_4–CHO)_6$ **1-[G$_0$]** or the trialdehyde $S{=}P(O–C_6H_4–CHO)_3$. The sequence of reactions is depicted in Scheme 1, starting from the cyclotriphosphazene core **1-[G$_0$]**, which is readily prepared by reacting one equivalent of $N_3P_3Cl_6$ with six equivalents of the triethylammonium salt of 4-hydroxybenzaldehyde. The first step is a Schiff reaction between the core **1-[G$_0$]** and six equivalents of methylhydrazine, which affords compound **1-[G$_0'$]**. The second step consists of the grafting of six diphenylphosphine groups, which yields compound **1-[G$_0''$]**. The third and last step of the reiterative process is a Staudinger reaction between the aminophosphine groups of **1-[G$_0''$]** and the azide function of the dialdehyde **2** which creates phosphorus nitrogen double bonds. The first generation of the dendrimer thus obtained, **1-[G$_1$]**, possesses 12 aldehyde groups, whereas the core had only six. The repetition of this sequence of three reactions, using alternatively methylhydrazine, diphenylchlorophosphine and the azide **2** provides the second generation **1-[G$_2$]**, then the third generation **1-[G$_3$]**. This latter dendrimer possesses 48 aldehyde end groups, and it is the last one obtained in this series (Fig. 2). Indeed, the very poor solubility of dendrimer **1-[G$_3$]** precludes any attempt to go further in the building of this series of dendrimers.

Each step of the synthesis has been characterized by ^{31}P NMR at 81.01 MHz for the lowest generation and 32.43 MHz for the highest generation, this latter field inducing a better separation of the doublets (Fig. 3). The spectra of dendrimers **1-[G$_n''$]** ($n=0$–2) display, beside the signals of the inner layers, a singlet at $\delta=$ 67.7 ppm corresponding to the aminophosphine end groups. The Staudinger reaction (**1-[G$_n''$]**→**1-[G$_{n+1}$]**, $n=0$–2) induces in all cases the total disappearance of this signal with the appearance of two doublets at $\delta=22$ ppm (Ph_2P groups) and $\delta=48.7$ ppm ($P{=}S$ groups) with a coupling constant $^2J_{PP}=34$ Hz. Remarkably, all the layers of phosphorus atoms of the third generation dendrimer **1-[G$_3$]** are distinguishable. Indeed, the spectrum of **1-[G$_3$]** consists of one singlet for the three phosphorus of the cyclotriphosphazene core P_0 and three sets of two doublets corresponding to the $Ph_2P{=}N–P{=}S$ moieties of the first, second and third generation (Fig. 3).

Analogous experiments carried out from the cyclotriphosphazene core using the chlorodiazaphospholane **3** instead of chlorodiphenylphosphine afford compounds **4-[G$_0''$]** and **4-[G$_1$]** (Scheme 2).



Scheme 1. Synthesis of a dendrimer via the reiteration of a sequence of three reactions

We have also applied these reactions starting from the trialdehyde core $S{=}P(O{-}C_6H_4{-}CHO)_3$, and using chlorodiphenylphosphine. The synthesis has been stopped at the third generation, due to the problems of insolubility already encoun-

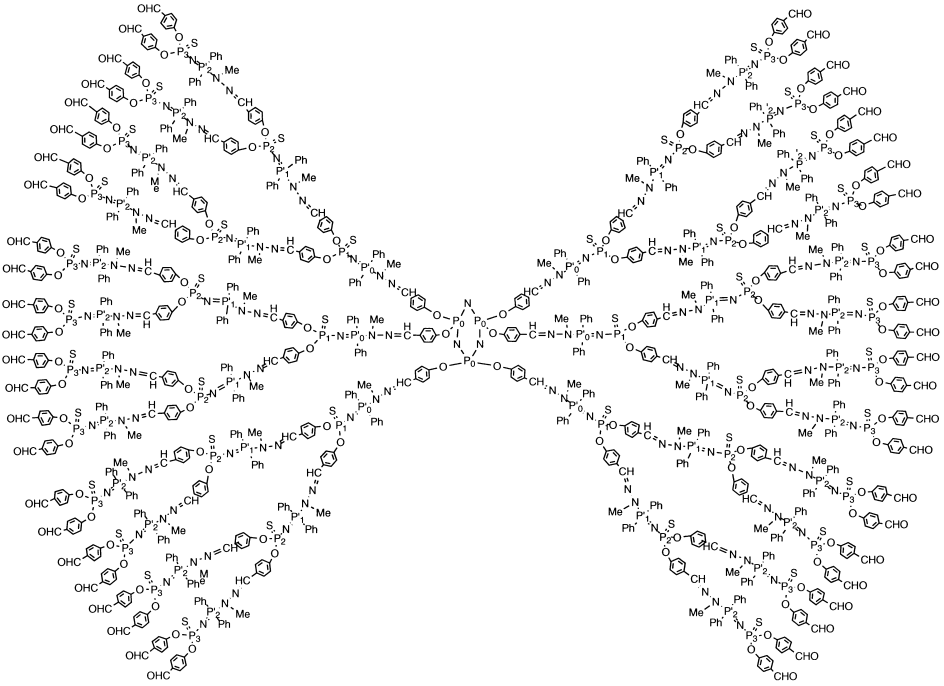


Fig. 2. Third generation of the dendrimer **1-[G$_3$]**, showing the numbering used for phosphorus atoms.

tered with the cyclotriphosphazene core. Dendrimer **5-[G$_3'$]**, which is the last one characterized in this series, possesses 24 aminophosphine end groups (Fig. 4).

2.2. Phosphine groups grafted on the surface of dendrimers

2.2.1. Synthesis of the dendrimer

The second way to synthesize phosphorus-containing dendrimers is more convenient than the previous one, since it necessitates only two steps to build one generation [27]. Scheme 3 displays the synthesis from $P(S)Cl_3$ as core. The first step is a nucleophilic substitution reaction of 4-hydroxybenzaldehyde on $P(S)Cl_3$, to afford the trialdehyde **6-[G$_0'$]**, which was used as core in the previous synthesis. The second step is a Schiff reaction between the aldehyde functions and the phosphorohydrazide **7a**, obtained by reacting methylhydrazine with $P(S)Cl_3$ at low temperature. The condensation affords quantitatively the first generation of the dendrimer **6-[G$_1$]**, which possesses six chlorine atoms, whereas the core had only three. The repetition of the reaction with hydroxybenzaldehyde sodium salt, then phosphorohydrazide **7a**, gives the second generation **6-[G$_2$]**. In order to make sure of the reactivity of all the terminal functions, the reactions are left overnight, even though the reactions are complete within 2 h. Furthermore, a slight excess of reagents is used and very easily removed by washing. In these conditions, the reiterative process has been

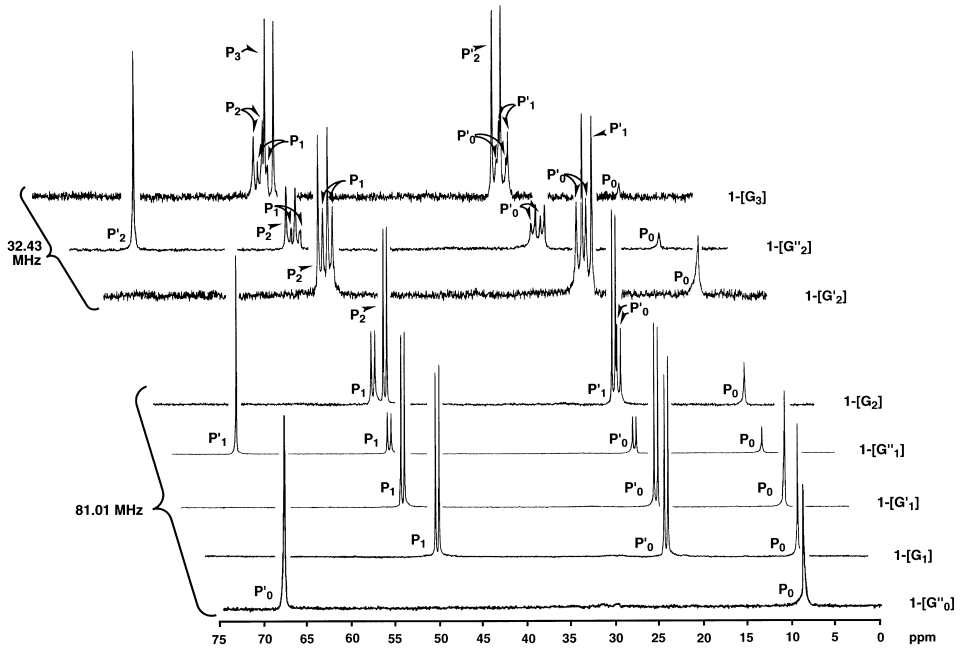
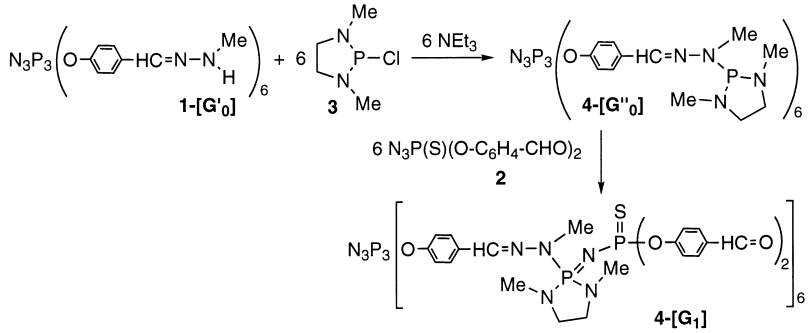


Fig. 3. ^{31}P NMR spectra of dendrimers **1-[G$_0''$]**–**1-[G$_2$]** (81.01 MHz) and **1-[G$_2'$]**–**1-[G$_3$]** (32.43 MHz) (see Fig. 2 for the numbering used).



Scheme 2. Synthesis of a dendrimer incorporating diazaphospholane rings

carried out to the twelfth generation. Dendrimer **6-[G$_{12}$]** thus obtained possesses theoretically 12 288 Cl atoms on the surface, and it is still soluble in several organic solvents such as THF or dioxane. This compound is the highest generation ever synthesized for a dendrimer, and it is also the last one obtainable in this series. Indeed, the surface of the next generation would be overcrowded, and an attempt to react the hydroxybenzaldehyde sodium salt with **6-[G$_{12}$]** gave only an insoluble material [28].

As seen previously for dendrimer **1-[G$_n$]**, every step of the synthesis of dendrimer

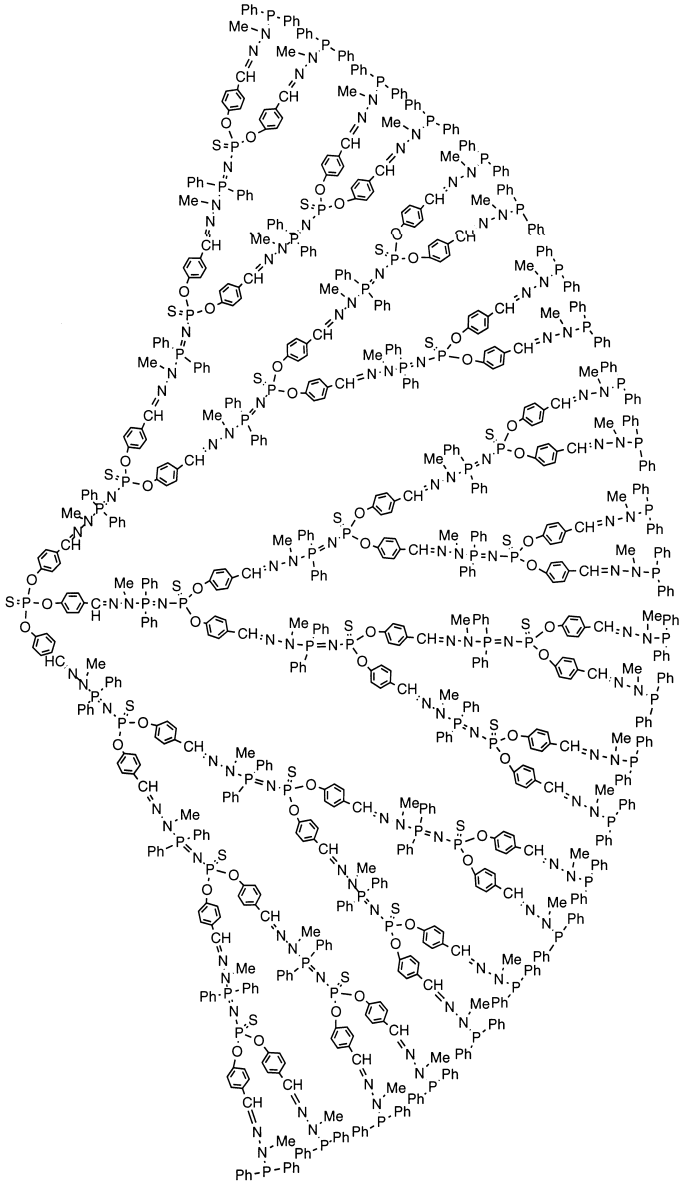
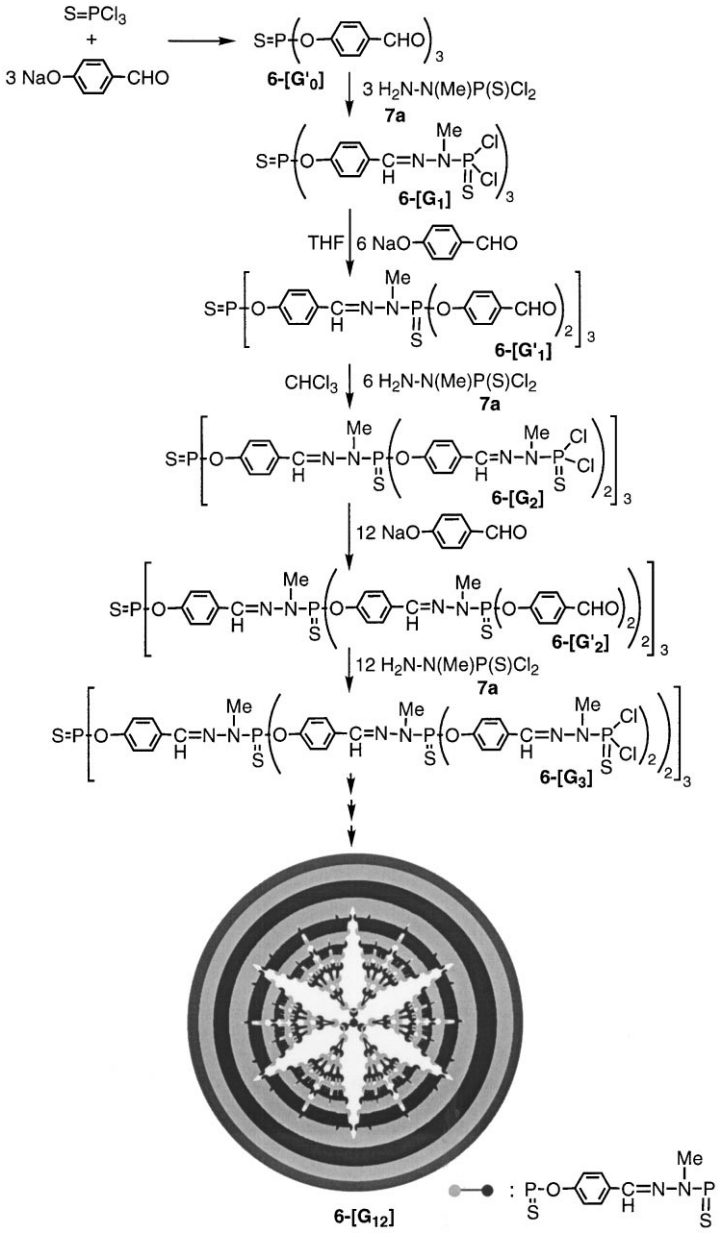


Fig. 4. Third generation of the dendrimer **5-[G$_3''$]**.

6-[G$_n$] can be rigorously monitored by ^{31}P NMR (Fig. 5). Indeed, the grafting of hydroxybenzaldehyde on $P_n(S)Cl_2$ groups (**6-[G$_n$]→6-[G$_n'$]**, $n=0$–11) induces in all cases the total disappearance of the signal corresponding to the $P_n(S)Cl_2$ end groups ($\delta^{31}P \cong 63$ ppm) with the appearance of a new signal corresponding to the $P_n(S)(OC_6H_4CHO)_2$ end groups, which are slightly shielded ($\delta^{31}P \cong 60$ ppm). The



Scheme 3. Synthesis of dendrimers up to generation 12 via the reiteration of a sequence of two reactions

condensation reaction (**6-[G′$_n$]→6-[G$_{n+1}$]**, $n=0$–11) is characterized in ^{31}P NMR spectra by the disappearance of the signal at $\delta^{31}P \cong 60$ ppm, and by the appearance of two new singlets: one at $\delta^{31}P \cong 61.5$ ppm, corresponding to the phosphorus of

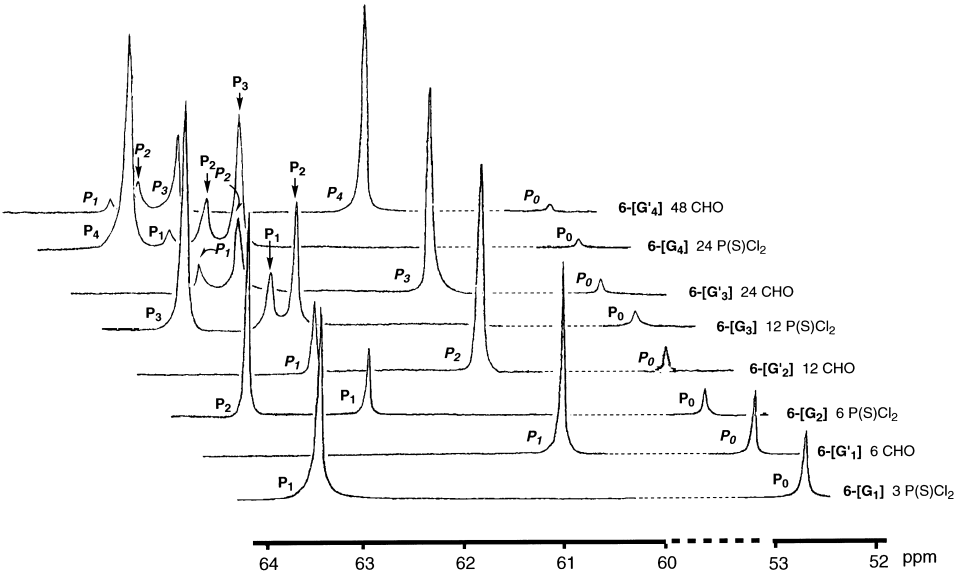


Fig. 5. ^{31}P NMR spectra of dendrimers **6-[G_n]** and **6-[G'_n]**.

the *n*th layer, and one at $\delta^{31}P \cong 63$ ppm corresponding to the $P_{n+1}(S)Cl_2$ end groups newly grafted on the surface. The relative intensity of these signals is approximately in the expected 1/2 ratio. The signal corresponding to each layer is distinguishable to generation 4 (Fig. 5). Starting from generation 5, a partial overlap is observed for the signals of the internal layers. However, in all cases, at least three signals, corresponding to the most external layers, are distinguishable, and the phenomena of shielding and deshielding of the signal, depending on the step considered, are observed to the twelfth generation. The signal of the core (P_0) is detected to the sixth generation: in this case, the ratio of the number of phosphorus P_0/P_6 is 1/96. This ratio indicates that the precision of the technique used is 1–2%. Thus defects in the construction of the dendrimers can be detected with this precision.

The reiterative process of synthesis, applied to the cyclotriphosphazene core, leads to a new series of dendrimers **8-[G_n]** which possess twice the number of terminal functions when compared to **6-[G_n]** at the same generation. In this case, the synthesis has been carried out to the eighth generation **8-[G'_8]** (1536 aldehyde end groups, theoretically) (Fig. 6), but it is not the last generation obtainable [29].

We have experimented with other modifications of the synthesis, for instance the use of $H_2NNMeP(O)Cl_2$ **7b** instead of **7a**. This phosphorohydrazide allowed us to introduce P=O groups instead of P=S groups when and where wanted during the synthesis of the dendrimer. Compound **7b** and hydroxybenzaldehyde were also used to build dendrimers with P=O groups at all the junctions of the dendrimer to generation four [30]. We have also synthesized dendrimers with P=S groups at all the junctions of the inner layers and P=O groups only on the surface, to generation seven [31], and the alternative use of **7a** and **7b** allowed us to isolate the first "layer-

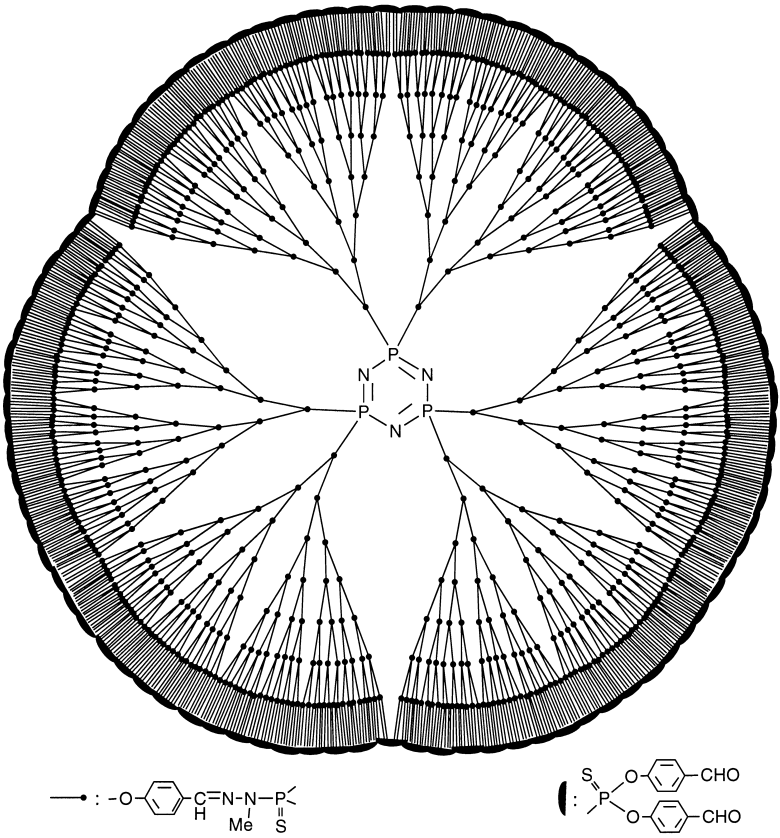


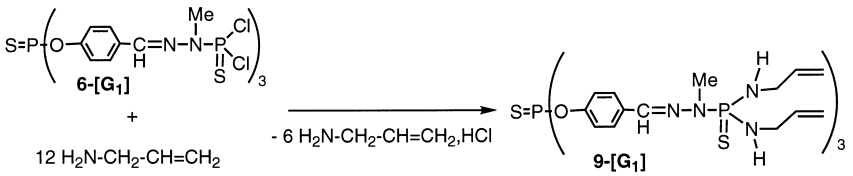
Fig. 6. Schematic drawing of the eighth generation of the dendrimer **8-[G$_8'$]**.

block'' dendrimer built with a regular alternation of two types of repeat units to the fourth generation **9-[G$_4$]** [32].

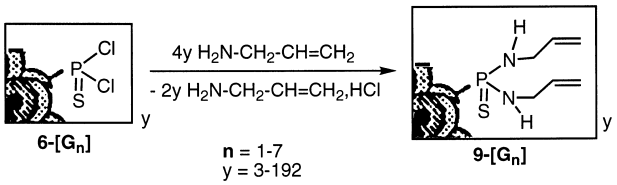
2.2.2. Grafting of phosphine groups on the surface of the dendrimer

Starting from the P(X)Cl$_2$ (X = O, S) or aldehyde end groups, we have developed a versatile chemistry [30,31,33–39], which allowed us to graft many types of organic, bioorganic, or phosphorus-containing groups. Among them, the most interesting is certainly the grafting of diphenylphosphine groups, using a Mannich type reaction. This reaction requires us first to graft NH groups on the surface of the dendrimer. This requirement has been fulfilled, reacting primary amines on the P(S)Cl$_2$ end groups, or hydrazines on the aldehyde end groups.

Thus, reaction of 12 equivalents of allylamine with dendrimer **6-[G$_1$]** affords compound **9-[G$_1$]** which possesses six NH(allyl) groups (Scheme 4). This reaction, which has been applied to the seventh generation to afford dendrimer **9-[G$_7$]** [35], is depicted in Scheme 5. Note that only one terminal function of the dendrimer is represented, which symbolizes all the terminal functions.



Scheme 4. Grafting of allylamine groups on the surface of a dendrimer of generation 1



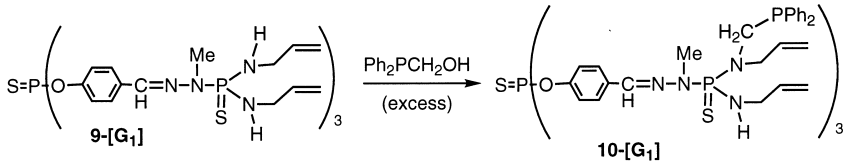
Scheme 5. Grafting of up to 384 allylamine rings

The last step to graft diphenylphosphine groups on the surface of the dendrimer is a Mannich type reaction, using Ph_2PCH_2OH. The condensation reaction between **9-[G$_1$]** and Ph_2PCH_2OH, heated at 80 °C, leads to dendrimer **10-[G$_1$]**, which is obtained by a specific functionalization of the surface [40]. Indeed, only one Ph_2PCH_2 group is grafted on each P(S)(NHallyl)$_2$ group, even when an excess of Ph_2PCH_2OH is used (Scheme 6). This particular behavior is proven by FAB mass spectrometry. It is also easily seen on the ^{31}P NMR spectrum of **10-[G$_1$]**, which displays two doublets at $\delta = -21$ ppm and $\delta = 72$ ppm ($^3J_{PP} = 5$ Hz), the former corresponding to the PPh_2 moieties and the latter to the P(S) groups. The signal of the P(S) groups should have been a triplet if both NH groups were reacted with Ph_2PCH_2OH, thus the occurrence of a doublet unambiguously proves that only one NHallyl group has reacted on each P(S)(NHallyl)$_2$ group.

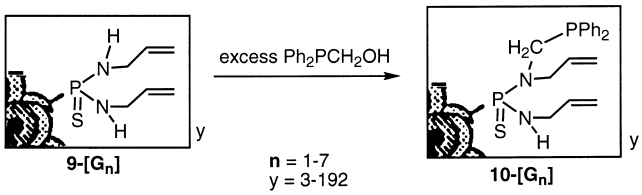
The same experiments have been carried out to the seventh generation **10-[G$_7$]** (Scheme 7). In all cases, the ^{31}P NMR spectra indicate that only one Ph_2PCH_2 group is grafted on each P(S)(NHallyl)$_2$ end group, with the occurrence of two doublets for the P–N–CH_2–P linkage.

All these experiments have also been used starting from the cyclotriphosphazene core **8-[G$_n$]** to the fourth generation to afford dendrimers **11-[G$_n$]** (Fig. 7).

Another way to graft NH groups on the surface of dendrimers consists of the condensation of hydrazines on dendrimers **6-[G$'_n$]** [35]. The reaction has been applied



Scheme 6. Specific grafting of phosphino groups on the surface of a dendrimer of generation 1



Scheme 7. Specific grafting of up up to 192 phosphino groups on the surface of dendrimers

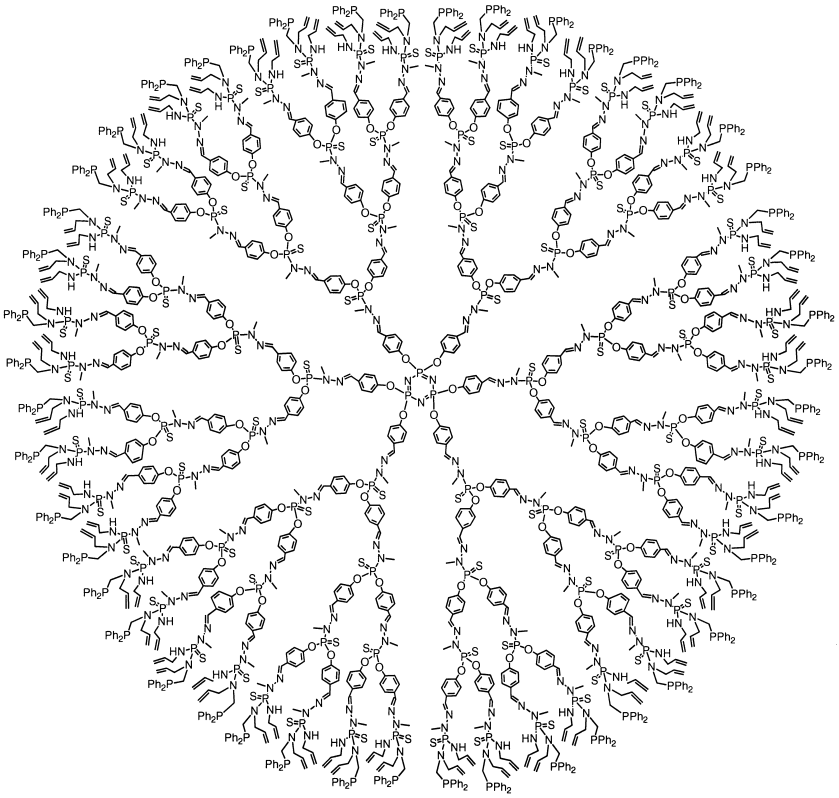
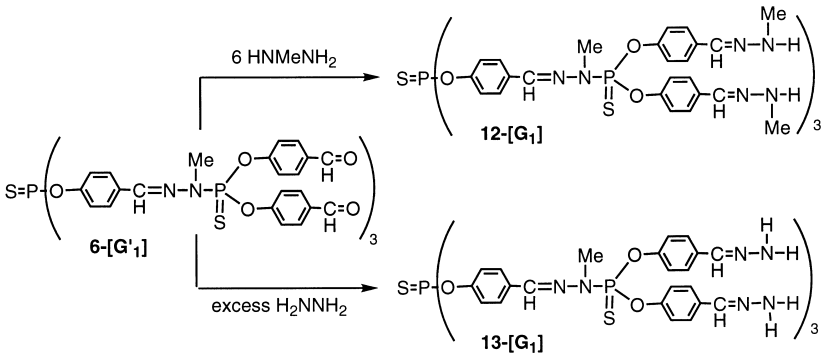
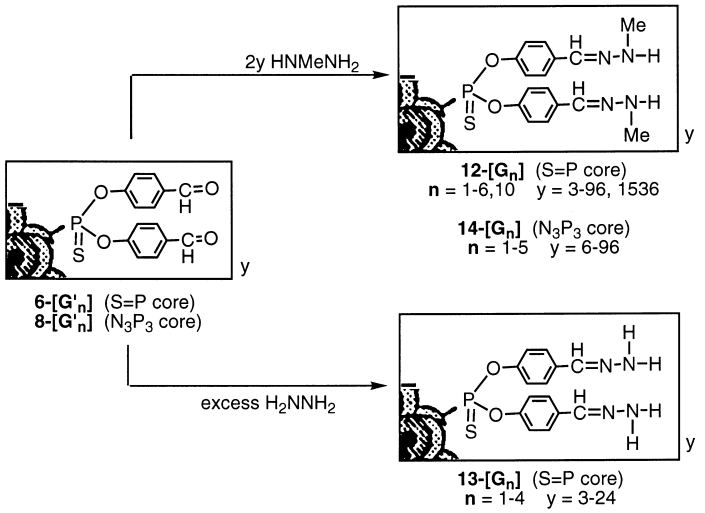


Fig. 7. Fourth generation of the dendrimer **11-[G_4]**.

to the first generation **6-[G_1']** with methylhydrazine, which affords dendrimer **12-[G_1]** (Scheme 8). The same condensation reaction is also used with hydrazine itself, provided a very large excess is used, in order to avoid coupling reactions between two arms or between two dendrimers (Scheme 8). These condensations have been applied to the tenth generation with methylhydrazine, which yields dendrimer **12-[G_{10}]** [41,42], and to the fourth generation with hydrazine, which yields dendrimer **13-[G_4]** [35,43] (Scheme 9). The condensation with methylhydrazine has



Scheme 8. Hydrozono terminated dendrimers of generation 1

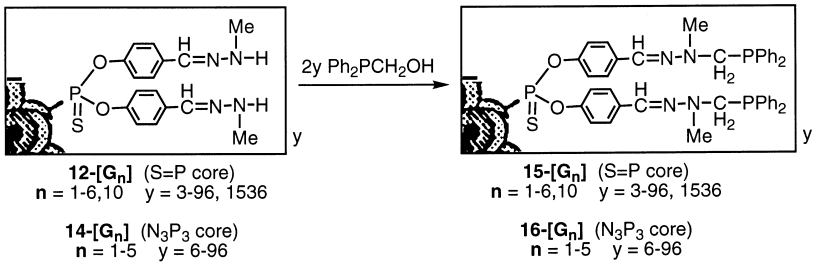


Scheme 9. Hydrazono terminated dendrimers of generations 1–10

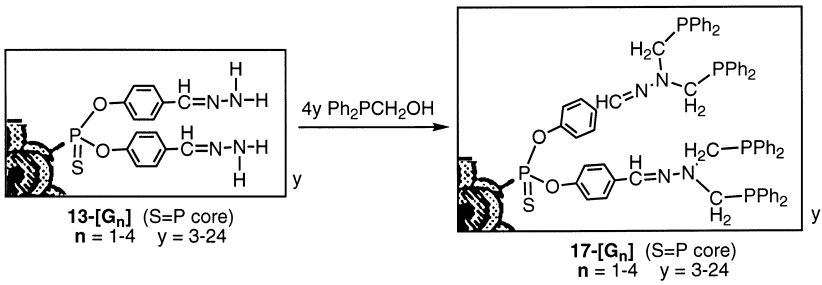
also been accomplished using dendrimers **8-[G′$_n$]** (cyclotriphosphazene core) to afford dendrimers **14-[G$_n$]** to the fifth generation [41,44] (Scheme 9).

The Mannich type reaction applied to dendrimers **12-[G$_n$]** affords dendrimers **15-[G$_n$]** ($n=1$–6, 10) which possess up to 3072 phosphine groups on the surface for the tenth generation (Scheme 10) [41,42]. The obtained dendrimer **15-[G$_{10}$]** indicates that steric hindrance does not affect the reactivity of the surface functions. To the best of our knowledge, this dendrimer is the largest polyphosphine of a well-defined structure ever reported. Dendrimers **16-[G$_n$]** ($n=1$–5) are obtained in the same way, using dendrimers **14-[G$_n$]**, built from the cyclotriphosphazene core (Scheme 10) [41,44].

Compounds **13-[G$_n$]** are precursors of the diphosphine-terminated dendrimers **17-[G$_n$]** (Scheme 11). Indeed, the presence of NH_2 end groups allowed us to graft



Scheme 10. Phosphino terminated dendrimers of generations 1–10



Scheme 11. Diphosphino terminated dendrimers of generations 1–4

two diphenylphosphine groups on each primary amine, giving rise to the formation of potentially bi- (or tri-) dentate P–CH_2–N–CH_2–P linkages to the fourth generation (Fig. 8) [35,43,45].

The last method we have used to graft phosphines on the surface of dendrimers necessitates three steps from the aldehyde end groups (Scheme 12) [46]. The first step is the condensation with chiral methylbenzylamine (R and S separated isomers) to afford **18R-[G_n]** and **18S-[G_n]**. Then, dendrimers **19R-[G_n]** and **19S-[G_n]** are obtained when sodium cyanoborohydride is used to selectively reduce the imine bonds, without reducing the hydrazone bonds constituting the skeleton of the dendrimer. The third step is again a Mannich reaction between Ph_2PCH_2OH and the NH groups created by the reduction. Dendrimers **20R-[G_n]** and **20S-[G_n]** thus obtained possess up to 48 diphenylphosphine groups linked to chiral substituents (Fig. 9).

3. Complexation properties of phosphine-terminated dendrimers

We have studied the complexation ability of most of the phosphine-terminated dendrimers described above, with emphasis on the reactivity of diphenylphosphine groups grafted on methylhydrazone or hydrazone end groups (compounds **15-[G_n]**, **16-[G_n]** and **17-[G_n]**). However, first attempts were carried out with the

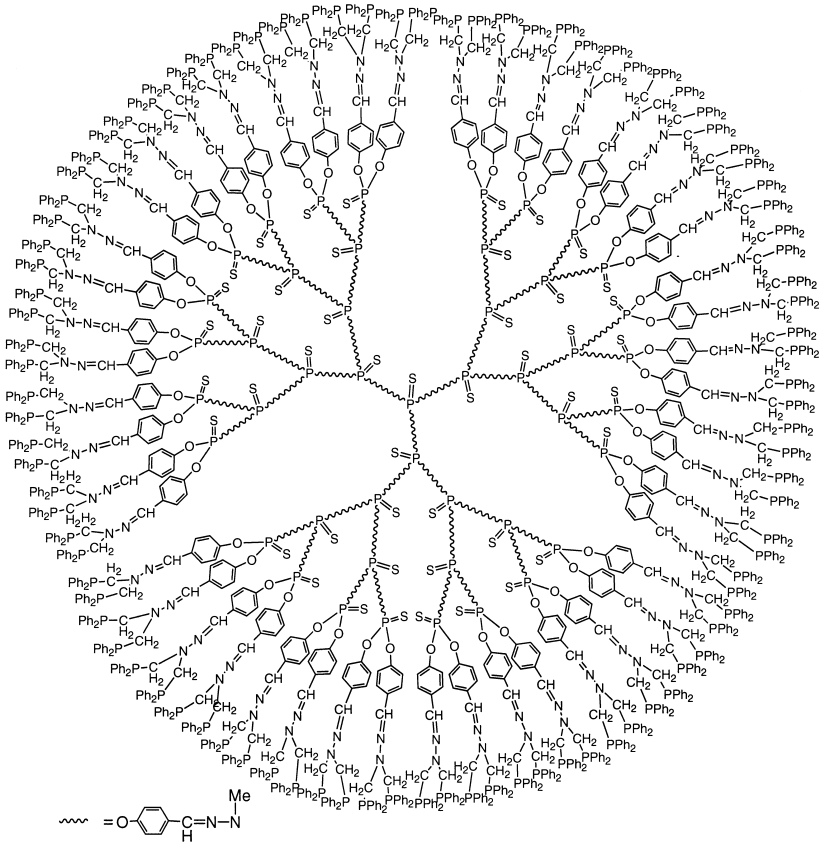


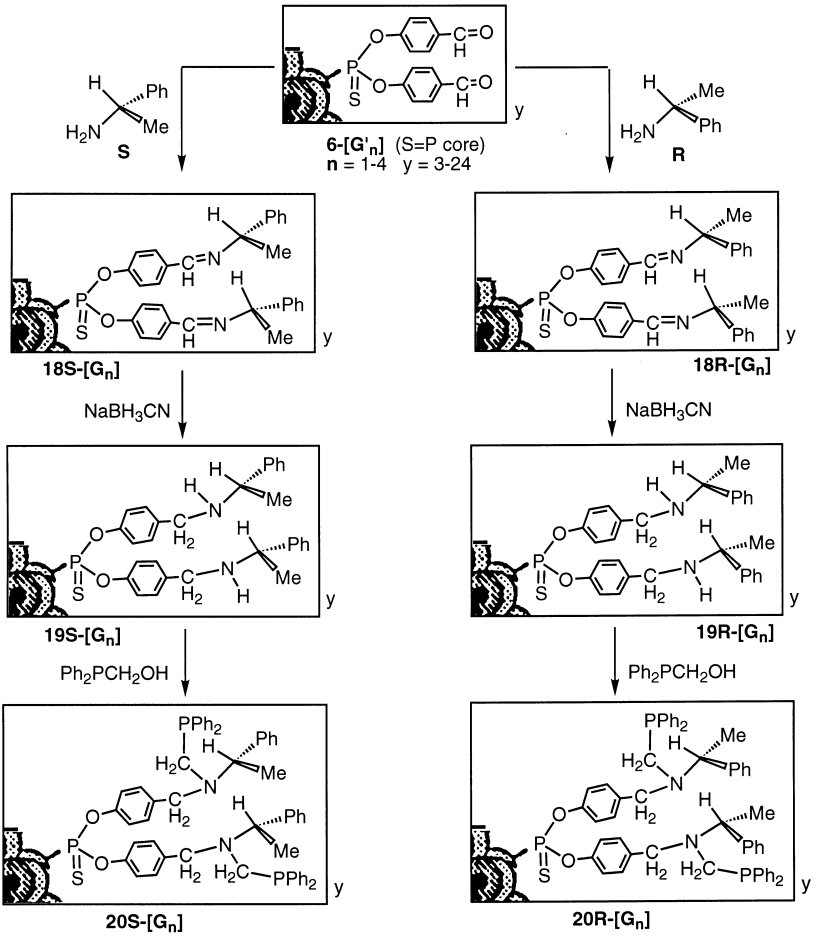
Fig. 8. Fourth generation of the dendrimer **17-[G$_4$]**.

aminophosphine end groups of dendrimers **1-[G$_n''$]** and diiron nonacarbonyl, leading for instance to complex **21-[G$_0''$]** (Scheme 13).

Dendrimers **10-[G$_n$]** ($n \leqslant 2$) also behave classically toward $Fe_2(CO)_9$ or $W(CO)_5(THF)$ to give dendrimers **22-[G$_n$]** and **23-[G$_n$]**, respectively (Scheme 14). These compounds are characterized by ^{31}P NMR which shows the expected deshielding of the Ph_2P signal: $\delta \cong 68$ ppm for **22-[G$_n$]**, and $\delta \cong 16$ ppm for **23-[G$_n$]** with the presence of satellites ($^1J_{PW} \cong 233$ Hz), instead of $\delta \cong -21$ ppm for **10-[G$_n$]**. According to ^1H and ^{13}C NMR, the allyl groups are not involved in the complexation [40].

3.1. Complexation properties of phosphines grafted on methylhydrazone end groups

We tested first the reactivity of dendrimers **15-[G$_n$]** and **16-[G$_n$]** toward two very common transition metal derivatives, $Fe_2(CO)_9$ and $W(CO)_5(THF)$. Complexation has been carried out with dendrimers **15-[G$_n$]** (P=S core) to the fifth generation with iron (**24-[G$_5$]**: 96 $Ph_2P \rightarrow Fe(CO)_4$ end groups), and to the fourth generation



Scheme 12. Stereogenic imino, amino and aminophosphino chain ends dendrimers

with tungsten (**25-[G$_4$]**: 48 $Ph_2P{\rightarrow}W(CO)_5$ end groups) (Scheme 15, Fig. 10) [42]. These experiments have been carried out only on the first generation of dendrimer **16-[G$_n$]** which affords compounds **26-[G$_1$]** and **27-[G$_1$]** with iron and tungsten, respectively (Scheme 15) [44]. In all cases, the complexation occurs readily at room temperature within a few hours. The reaction is monitored by ^{31}P NMR which shows the deshielding of the Ph_2P groups from $\delta \cong -23$ ppm for **15-[G$_n$]** and **16-[G$_n$]** to $\delta \cong 52$ ppm for the $Ph_2P{\rightarrow}Fe(CO)_4$ end groups of **24-[G$_n$]** and **26-[G$_1$]**, and $\delta \cong 16$ ppm for the $Ph_2P{\rightarrow}W(CO)_5$ end groups of **25-[G$_n$]** and **27-[G$_1$]**.

These first complexation experiments with M(0) derivatives have then been extended to various M(I) derivatives, mainly gold(I) and rhodium(I) compounds. The reaction of AuCl(tht) (tht = tetrahydrothiophene) with dendrimers **15-[G$_n$]** (n = 1, 4–6, 10) and **16-[G$_n$]** (n = 1, 3–5) occurs readily at room temperature, even for the tenth generation, to afford dendrimers **28-[G$_n$]** (n = 1, 4–6, 10) [41,42] and

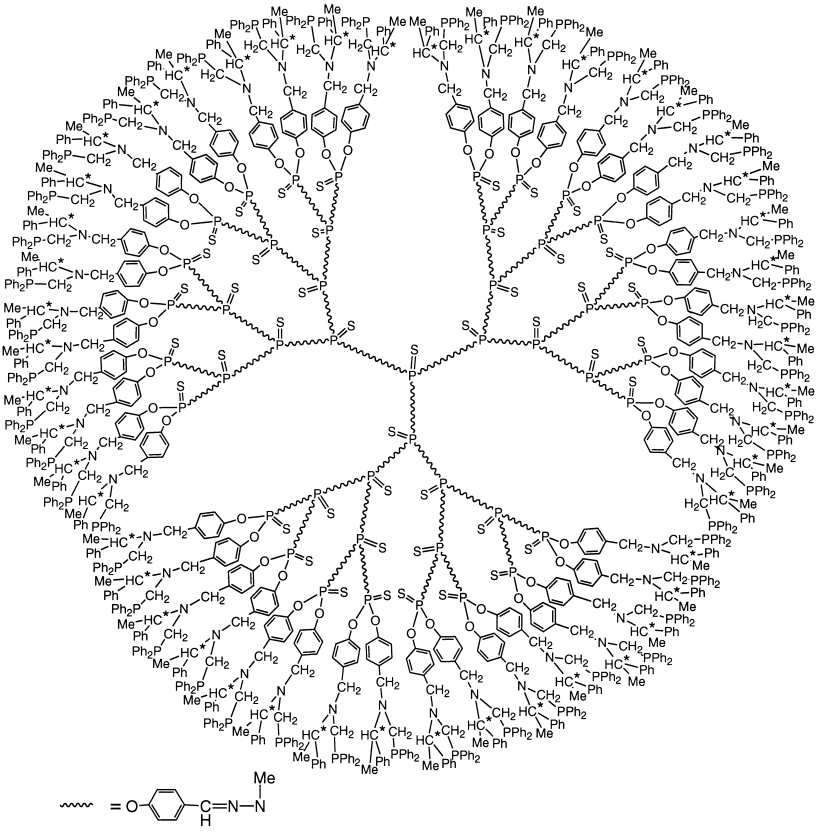
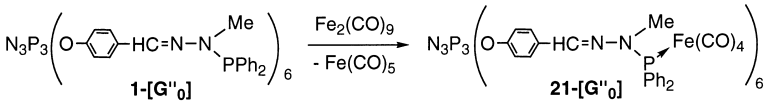


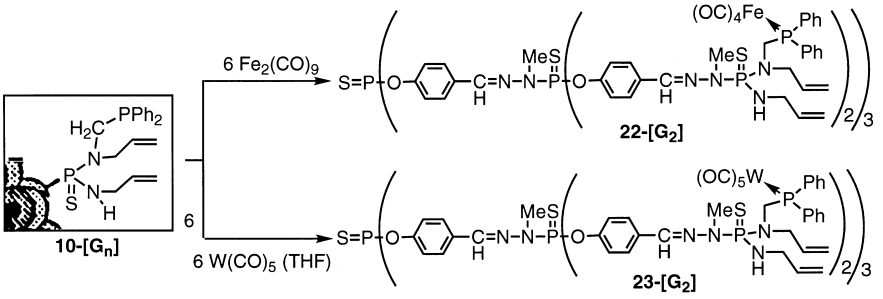
Fig. 9. Fourth generation of the chiral dendrimer **20-[G$_4$]**.



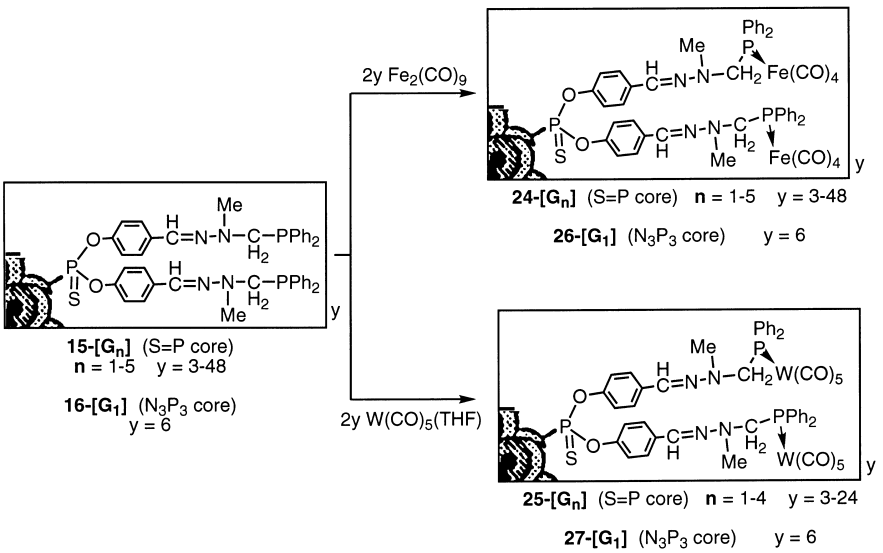
Scheme 13. Complexation of terminated amino phosphino groups with $Fe_2(CO)_9$

29-[G$_1$] ($n=1$, 3–5) [41,44], respectively (Scheme 16). The complexation induces the expected deshielding effect in ^{31}P NMR spectra, with the occurrence of a singlet at $\delta \cong 21$ ppm corresponding to the $Ph_2P \rightarrow AuCl$ end groups of **28-[G$_n$]** and **29-[G$_n$]**.

The presence of such a high number of gold atoms on the surface (up to 3072 for **28-[G$_{10}$]**) allows the imaging of dendrimers **28-[G$_n$]** and **29-[G$_n$]** by high resolution electron microscopy [41]. Experiments were carried out with **29-[G$_3$]**, **29-[G$_4$]** and **29-[G$_5$]**, to compare the size of consecutive generations, and with **28-[G$_{10}$]** to see the influence of the nature of the core on the shape of dendrimers. As shown in Fig. 11, isolated spheres of these four compounds were observed with diameters of 60 ± 5, 75 ± 5, 90 ± 5 and 150 ± 5 Å for **29-[G$_3$]**, **29-[G$_4$]**, **29-[G$_5$]** and **28-[G$_{10}$]**, respectively.



Scheme 14. Iron and tungsten metalla complexes formation



Scheme 15. Synthesis of metalladendrimers of generations 1–5

The presence of a chlorine atom bonded to gold should confer to these dendrimers a versatile reactivity. We have carried out only one experiment up to now, using Cp_2ZrMe_2 as alkylating reagent toward **28-[G$_4$]** and **29-[G$_1$]** (Scheme 16, Fig. 10). Compounds **30-[G$_4$]** and **31-[G$_1$]** are characterized by the presence of a doublet for the Me–Au–P groups in ^{1}H NMR spectra ($^3J_{HP} = 8$ Hz) [42,44].

The complexation of rhodium(I) derivatives with dendrimers **15-[G$_n$]** and **16-[G$_n$]** also occurs readily at room temperature. For instance, the reaction of the dimer $[RhCl(COD)]_2$ (COD = cyclooctadiene) affords dendrimers **32-[G$_n$]** (P=S core, $n = 1, 4$) [42] and **33-[G$_n$]** (N_3P_3 core, $n = 1$–4) [44], respectively (Scheme 17, Fig. 10). The complexation is demonstrated by the presence of a doublet in ^{31}P NMR spectra at $\delta \cong 23$ ppm ($^1J_{PRh} \cong 149$ Hz) corresponding to the $Ph_2P \rightarrow RhCl(COD)$ end groups. Other experiments have been carried out starting from $Rh(acac)(CO)_2$ (acac = acetylacetonate) and dendrimers **15-[G$_n$]** ($n = 1$, 4–6) (Scheme 17, Fig. 10).

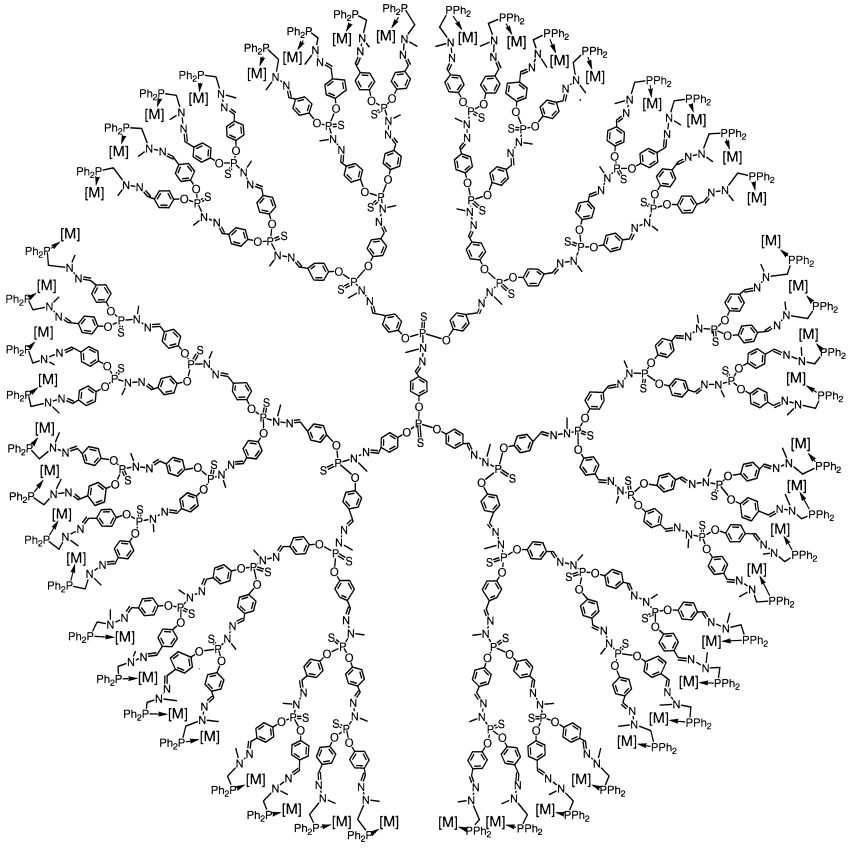
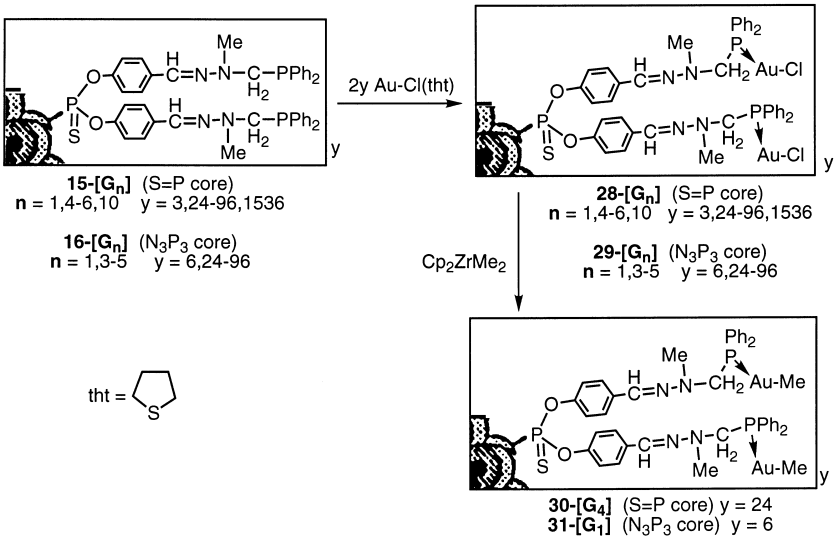


Fig. 10. Fourth generation of the phosphine-terminated dendrimer complexes **24-[G_4]**, **25-[G_4]**, **28-[G_4]**, **30-[G_4]**, **32-[G_4]**, **34-[G_4]**.

Dendrimers **34-[G_5]** and **34-[G_6]** are poorly soluble, but they are characterized, as well as **34-[G_1]** and **34-[G_4]**, by ^{31}P NMR. Indeed, the complexation is unambiguously confirmed by the appearance of a doublet at $\delta \cong 41$ ppm ($^1J_{PRh} \cong 175$ Hz) corresponding to the $Ph_2P \rightarrow Rh(acac)(CO)$ end groups [42].

3.2. Complexation properties of diphosphine end groups

Dendrimers **17-[G_n]** possess $Ph_2PCH_2NCH_2PPh_2$ linkages which can act as chelates toward various transition metal derivatives possessing a four electron donor leaving group. Indeed, one can expect that the formation of six-membered rings will be much more favored than the complexation between two arms or two dendrimers.



Scheme 16. Gold complexation on the surface of dendrimers (generations 1, 4, 6, 10)

We have carried out our first experiments with cyclooctadiene as a leaving group. Thus, the reaction of Rh(acac)(COD) with dendrimers **17-[G$_n$]** affords the expected rhodium complexes **35-[G$_n$]** (Scheme 18) which are mainly characterized by the appearance of a doublet at $21.8 < \delta < 23.5$ ppm ($^1J_{PRh}$ from 130.8 to 131.2 Hz) in the ^{31}P NMR spectra of compounds **35-[G$_n$]**, corresponding to the $Ph_2P \rightarrow Rh(acac)$ groups [43]. The narrow linewidth of the signals confirms the formation of the expected six-membered ring instead of oligomers, even for the third generation **35-[G$_3$]** (Fig. 12).

Palladium-cyclooctadiene derivatives behave in the same way as the Rh(COD) derivatives [43]. For instance, the reaction of three equivalents of $PdCl_2$(COD) with the first generation dendrimer **17-[G$_1$]** affords compound **36-[G$_1$]** (Scheme 19). The expected deshielding effect is observed in the ^{31}P NMR spectrum for the PPh_2 moieties whose signal appears as a singlet at $\delta = -25.5$ ppm for **17-[G$_1$]** and at $\delta =$ 7.0 ppm for **36-[G$_1$]**. An easy halogen exchange occurs with KBr, leading to compound **37-[G$_1$]**, which is also directly prepared by reacting $PdBr_2$(COD) with **17-[G$_1$]**. Halogen exchange and alkylation on palladium simultaneously take place when **36-[G$_1$]** is treated with MeMgBr to afford compound **38-[G$_1$]**. This unsymmetrical bis(substituted) palladium complex is characterized by the occurrence of two doublets in the ^{31}P NMR spectra for the $Ph_2P \rightarrow PdMeBr$ groups at $\delta = -12.0$ ($^2J_{PP} = 43.3$ Hz, PPh_2 trans to Me) and $\delta = 18.2$ ppm ($^2J_{PP} = 43.3$ Hz, PPh_2 trans to Br).

Another unsymmetrical bis(substituted) palladium complex is formed starting from **36-[G$_1$]** and using Cp_2ZrMe_2 as alkylating agent. Compound **39-[G$_1$]** thus obtained is also isolated by reacting **17-[G$_1$]** with PdClMe(COD). This reaction has been applied to the second and third generations which afford dendrimers **39-[G$_2$]**

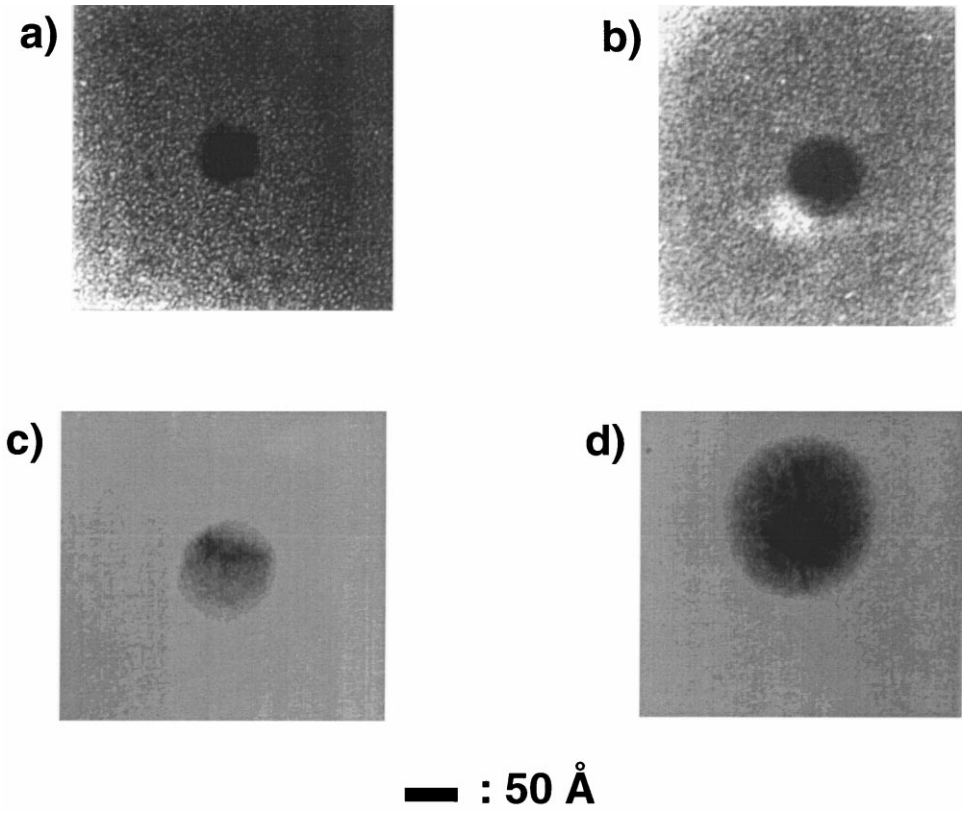
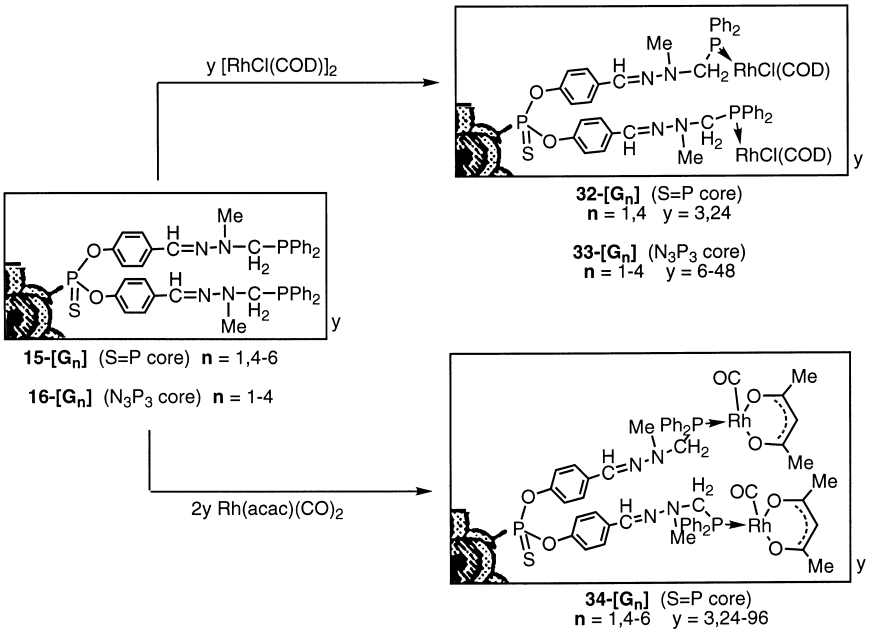


Fig. 11. Electron micrographs of dendrimers **29-[G$_3$]** (a), **29-[G$_4$]** (b), **29-[G$_5$]** (c) and **28-[G$_{10}$]** (d).

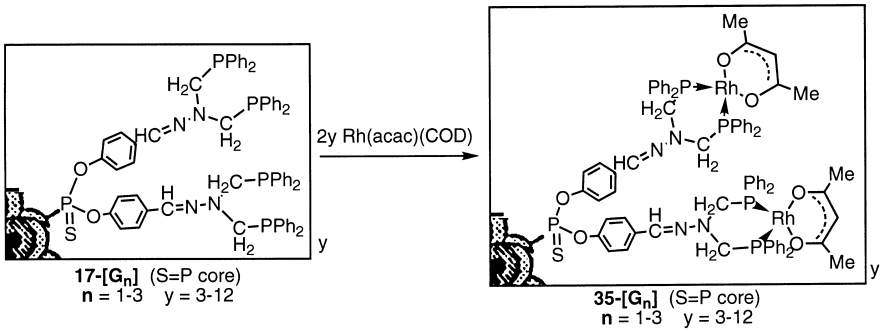
and **39-[G$_3$]**, respectively (Fig. 12). ^{31}P NMR spectra of dendrimers **39-[G$_n$]** are similar to that of **38-[G$_1$]**.

Insertion of carbon monoxide occurs in the Pd–Me bond of dendrimers **39-[G$_n$]**, leading to dendrimers **40-[G$_n$]**. The carbonylation induces a slight shielding of the signals of the PPh_2 groups from $\delta^{31}P \cong -13.9$ to -16.0 ppm (PPh_2 cis to Cl) and from $\delta^{31}P \cong 19.5$ to 5.2 ppm (PPh_2 trans to Cl), and the $^2J_{PP}$ coupling constant increases on going from the methyl derivatives **39-[G$_n$]** to the acetyl derivatives **40-[G$_n$]** from 40 to 72 Hz. Another insertion occurs in the Pd–C bond when dendrimers **40-[G$_1$]** and **40-[G$_2$]** are treated with norbornene (Scheme 19). The formation of the Pd-alkyl derivatives **41-[G$_1$]** and **41-[G$_2$]** induces in ^{31}P NMR spectra a decrease of the $^2J_{PP}$ coupling constant, and the occurrence of signals in areas close to those observed for **39-[G$_n$]**.

The reaction of dendrimers **17-[G$_n$]** with $PtCl_2$(COD) proceeds similarly as with the palladium derivatives, giving rise to compounds **42-[G$_n$]** ($n = 1$–3) (Scheme 20, Fig. 12) [43]. Besides signals corresponding to the phosphorus of the internal layers, the ^{31}P NMR spectra display a singlet at ca. -9 ppm for the $Ph_2P \rightarrow PtCl_2$ end



Scheme 17. Synthesis of Rh complexes from terminal phosphino groups



Scheme 18. Synthesis of Rh complexes from terminal diphosphino groups

groups with ^{195}Pt satellites ($^{1}J_{P^{195}Pt} \cong 3440$ Hz). Furthermore, a triplet is observed in the ^{195}Pt $\{^{1}H\}$ NMR spectrum, for example at $\delta = -4516$ ppm for **42-[G$_1$]**.

Alkylation of platinum with MeMgBr induces the substitution of all the chlorine atoms by methyl groups and yields compound **43-[G$_1$]** (Scheme 20). The ^{31}P NMR spectrum indicates the presence of only one compound, characterized by a singlet for the $Ph_2P \rightarrow PtMe_2$ groups at $\delta = -1.3$ ppm ($^{1}J_{P^{195}Pt} = 1795$ Hz). However, compound **43-[G$_1$]** is not stable in the presence of ClMgBr generated in the reaction. The evolution of **43-[G$_1$]** leads first to **44-[G$_1$]** (Scheme 20) as indicated by the ^{31}P NMR spectrum which displays two doublets ($^{2}J_{PP} = 17$ Hz) at $\delta = 0.0$ ppm

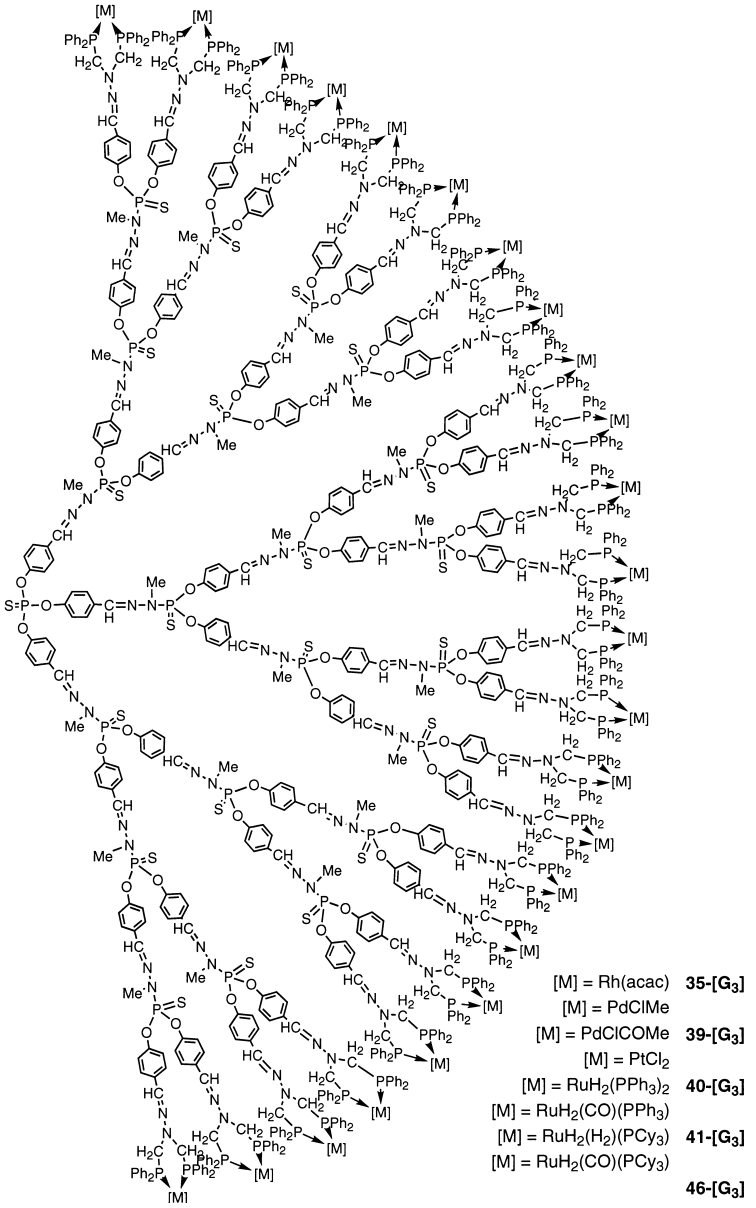
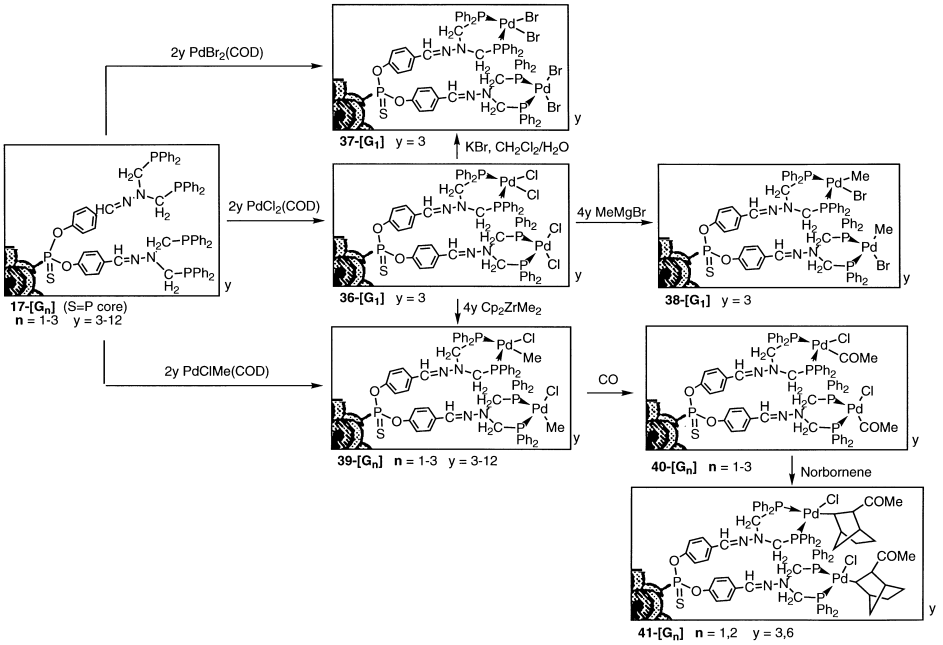


Fig. 12. Third generation of the diphosphine-terminated dendrimer complexes **35-[G_3]**, **39-[G_3]**–**41-[G_3]**, **46-[G_3]**–**50-[G_3]**.

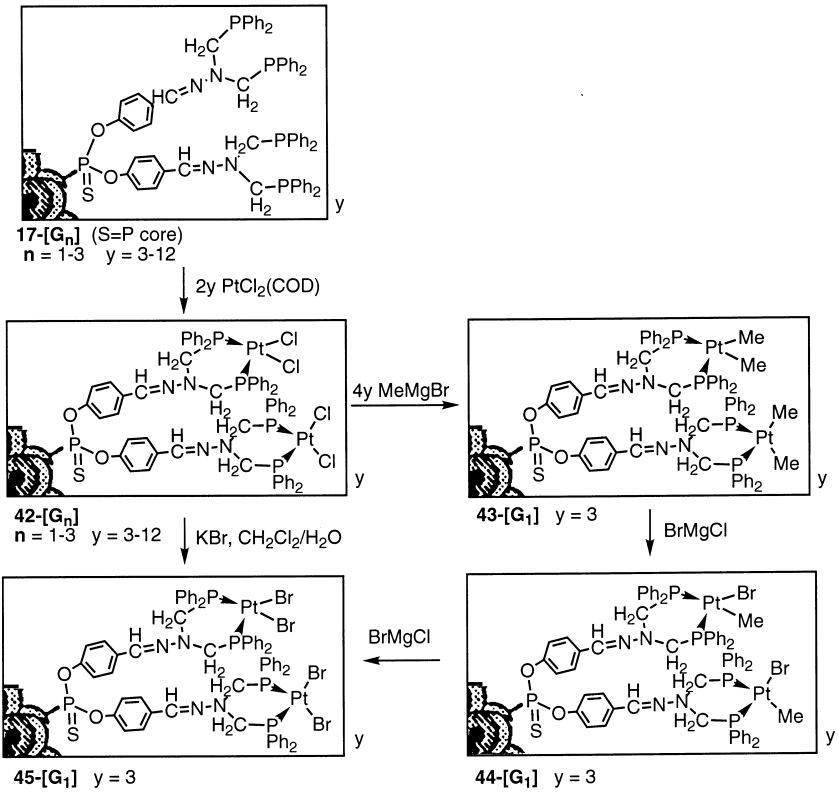
($^1J_{P^{195}Pt} = 4151$ Hz) and $\delta = -3.7$ ppm ($^1J_{P^{195}Pt} = 1673$ Hz), corresponding to two types of PPh_2 groups, due to the unsymmetrical substitution on platinum. The evolution of compound **44-[G_1]** leads slowly to **45-[G_1]**, which is also obtained when



Scheme 19. Synthesis of Pd complexes

KBr is reacted with **42-[G_1]**. The value of $^1J_{P^{195}Pt}$ (3363 Hz) is slightly different from the value obtained with **42-[G_1]** (3363 Hz), and a triplet is observed in the ^{195}Pt NMR spectra at $\delta = -4789$ ppm for **45-[G_1]** and $\delta = -4516$ ppm for **42-[G_1]**. These data indicate that halogens linked to platinum in compound **45-[G_1]** are bromine and not chlorine.

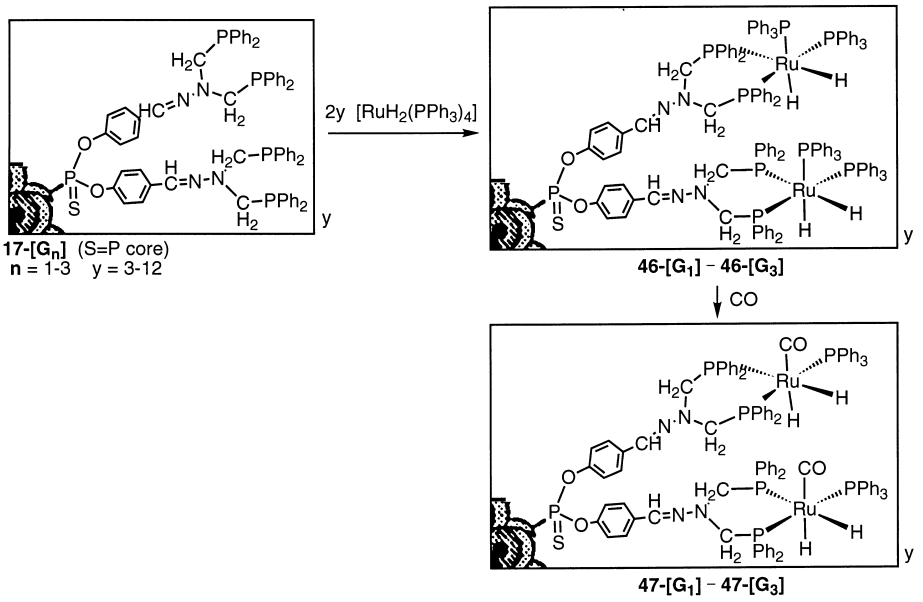
In order to get a deeper insight into the properties of the surface of diphosphine-terminated dendrimers, we have also studied the complexation of ruthenium hydride and dihydrogen derivatives, which are very sensitive to subtle electronic or steric modifications of their environment [45]. The reaction of $RuH_2(PPh_3)_4$ with dendrimers **17-[G_n]** leads to the substitution of two triphenyl phosphine ligands by the diphosphine end groups (Scheme 21). ^{31}P NMR spectra of dendrimers **46-[G_n]** (n = 1–3) thus obtained display complex patterns, very similar for the first and third generation, indicating that the size of dendrimers does not alter their electronic and steric properties, at least for relatively small generations (Fig. 13). Beside signals corresponding to the phosphorus of the internal layers (P_0, P_1, P_2, P_3 for the third generation), the four phosphine groups linked to ruthenium (P_A, P_B, P_C, P_D) appear as an ABMX spin system. The large value for the P_BP_D coupling constant (227 Hz) indicates a mutual trans arrangement of these atoms, whereas the small $^2J_{PP}$ coupling constant (19 Hz) observed for all the other signals indicates a cis arrangement for all the other substituents. The structure depicted in Scheme 21 and Fig. 13 is deduced from these data and from two-dimensional GE HMQC ^{1}H–^{31}P{^{31}P} experiments [45].



Scheme 20. Synthesis of Pt complexes

Complexes **46-[G$_n$]** are very stable, but they react slowly with carbon monoxide to give the corresponding carbonyl derivatives **47-[G$_n$]**. The structure of these compounds is again deduced from ^{31}P NMR spectra: the persistence of one large coupling constant ($^2J_{PP} = 231$ Hz) indicates that the PPh_3 group trans to PPh_2 is still linked to ruthenium, whereas the PPh_3 group cis to all the other phosphorus has been replaced by CO (Scheme 21).

The reaction of the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ with dendrimers **17-[G$_n$]** leads to a complex sequence of reactions (Scheme 22) [45]. Compounds **48-[G$_n$]** appear first, as indicated by the ^{31}P NMR spectrum (AX_2 pattern: 67.3 ppm (t, PCy_3), 38.7 ppm (d, PPh_2), $^2J_{PP} = 105$ Hz for **48-[G$_1$]**). After a few hours at room temperature, **48′-[G$_n$]** are formed and display a ^{31}P NMR pattern similar to that of **48-[G$_n$]** (66.9 ppm (t, PCy_3), 43.0 ppm (d, PPh_2), $^2J_{PP} = 102$ Hz for **48′-[G$_1$]**). Then, compounds **48-[G$_n$]** and **48′-[G$_n$]** disappear together with the appearance of two new compounds, **49-[G$_n$]** and **49′-[G$_n$]**, with a reduced P–P coupling constant when compared to that of **48-[G$_n$]** and **48′-[G$_n$]** ($^2J_{PP} = 15.4$ Hz for **49-[G$_1$]** and $^2J_{PP} = 21.1$ Hz for **49′-[G$_1$]**). This value indicates both the fluxionality of the molecule and the trans position of the PCy_3 ligand for **48-[G$_n$]** and **48′-[G$_n$]**, and the cis



Scheme 21. Synthesis of Ru complexes

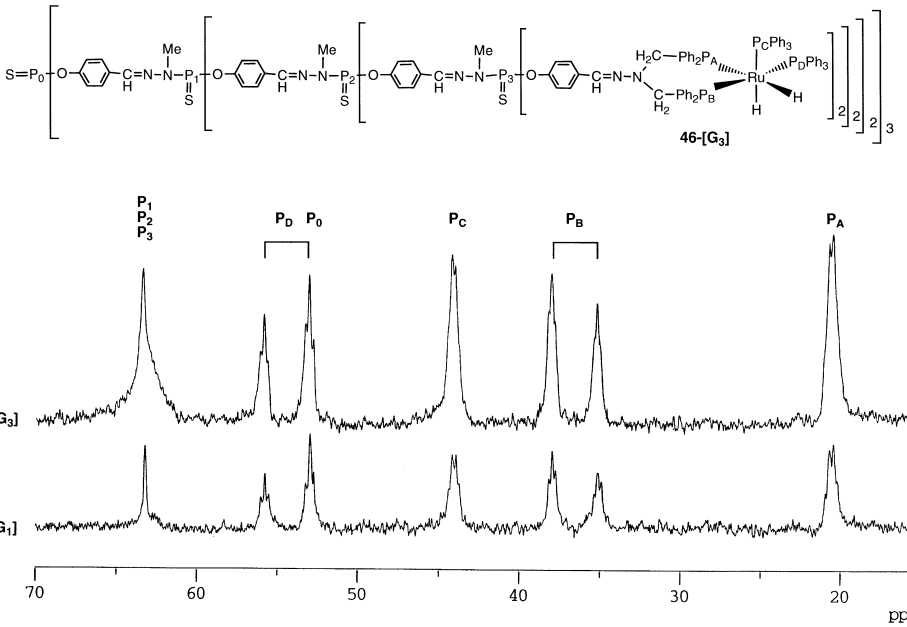
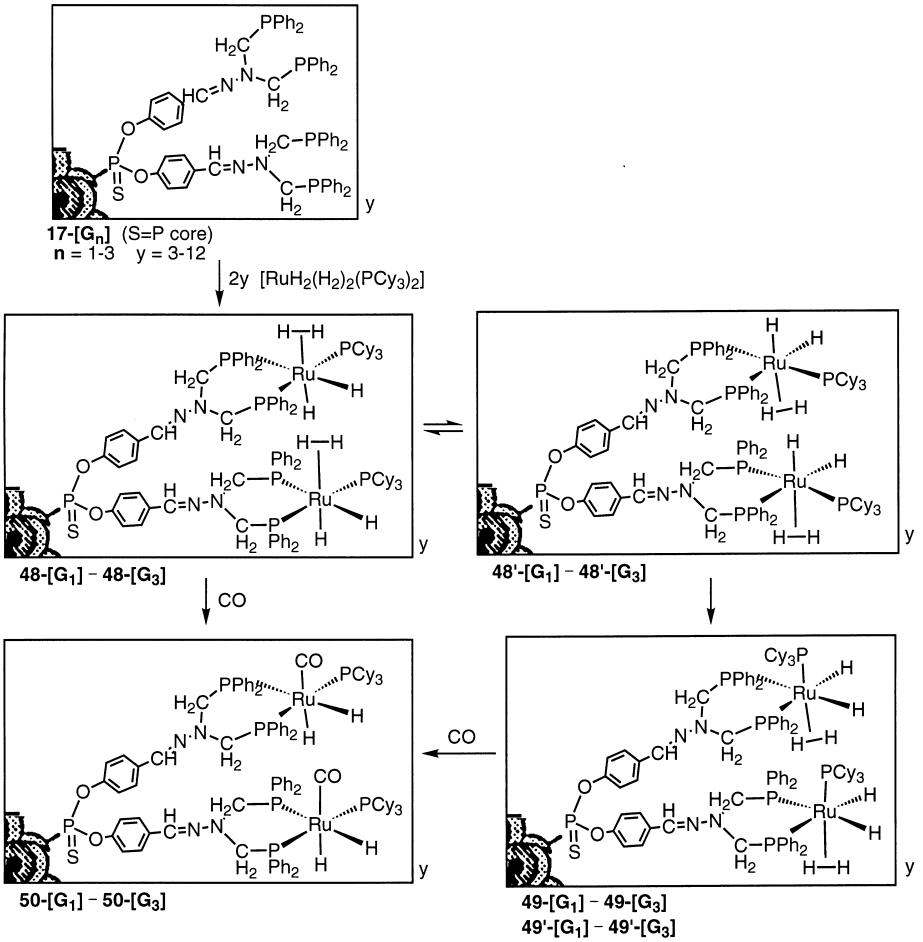


Fig. 13. ^{31}P NMR spectra of the ruthenium complexes **46-[G$_1$]** and **46-[G$_3$]**.



Scheme 22. Reaction of bis hydrogen complex $RuH_2(H_2)_2P(Cy_3)_3$ with dendrimers

position for **49-[G_n]** and **49′-[G_n]**. The formation of two isomers would have been easily understandable, due to the relative position of the phosphine groups, whereas the formation of four isomers is very surprising since all these compounds are fluxional. We believe that they correspond to different conformations of some functions of the dendrimers, the imino groups for instance. Addition of carbon monoxide (3 bar) to the **48-[G_n]**, **48′-[G_n]**, **49-[G_n]**, **49′-[G_n]** mixture leads specifically to the unique dihydrido cabonyl complexes **50-[G_n]**.

4. Conclusion

We have demonstrated that the grafting of phosphine groups on the surface of dendrimers, which has been accomplished to the tenth generation (3072 PPh_2

groups), leads to a versatile reactivity toward various metal complexes. Indeed, experiments have been carried out with Group 6 [$Ph_2P\rightarrow W(CO)_5$ end groups], Group 8 [$Ph_2P\rightarrow Fe(CO)_4$, $Ph_2P\rightarrow RuH_2(PPh_3)_2$ or $Ph_2P\rightarrow RuH_2(H_2)(PCy_3)$ end groups], Group 9 [$Ph_2P\rightarrow Rh(CO)(acac)$ or $Ph_2P\rightarrow Rh(Cl)(COD)$ end groups], Group 10 ($Ph_2P\rightarrow PdX_2$ or $Ph_2P\rightarrow PtCl_2$ end groups, X = Cl, Br), and Group 11 ($Ph_2P\rightarrow AuCl$ end groups) metals. In all cases, ^{31}P NMR has proved to be a unique and indispensable tool to characterize all these dendrimeric complexes, as well as their precursors. Furthermore, the grafting of gold on the surface allowed the imaging of dendrimers by electron micrographs to the tenth generation.

The reactivity of some of these complexes has also been studied. All these experiments prove that each arm of the dendrimer behaves independently, and that most of the reactions well-known for simple phosphines could be extended to phosphine-terminated dendrimers. In this perspective, it is obvious that catalysis will be one of the most important future prospects of this work.

Acknowledgements

The authors thank all their coworkers whose names appear in the references.

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