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Review

Phosphorus dendrimers possessing metallic groups in their internal structure (core or branches): Syntheses and properties

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Contents

Abstract

This review concerns metallic groups linked to the internal structure (core or branches) of phosphorus-containing dendrimers that are dendrimers possessing one phosphorus at each branching point. The synthetic aspect will be described first, ranked depending on the precise location of the metal: either at the core, or throughout the structure, or at one or several specific layers (layer-block type dendrimers), or in selected branches (segment-block type dendrimers). The second part concerns the properties of these metallo-phosphorus dendrimers, with emphasis on the information afforded by the metallic centers about the internal structure, and on the influence of the "burying" of a function inside a dendrimer on the properties of this function. The last part concerns the applications of some of these metallodendrimers in catalysis.

Keywords: Metallodendrimers; Layer-block dendrimers; Segment-block dendrimers; Phosphorus; Catalysis

1. Introduction

Metallodendrimers [1] constitute a very promising class of well-defined hyperbranched polymers, whose interest is mainly driven by their potential use as selective and recoverable homogeneous catalysts [2]. In many cases, the metallic centers are grafted to the periphery of the dendrimer, due to the simplicity of this synthetic method from a practical point of view [3]. However, a lot of examples are also known in which the metallic centers are located inside the dendritic structure [4], either at the core or within the branches (Fig. 1). In the latter case, the metallic groups may be found in the whole structure (B), or only at one (or several) specific layer (C, "layer-block dendrimer"), or only in some specific branches (D, "segment-block dendrimer"). In all cases, the metal can be linked either to the branching points, or located within the linkages constituting the branches. The properties of such dendrimers are expected to be different from those of dendrimers possessing metals as end groups, due in particular to a somewhat restricted access to the metallic centers.

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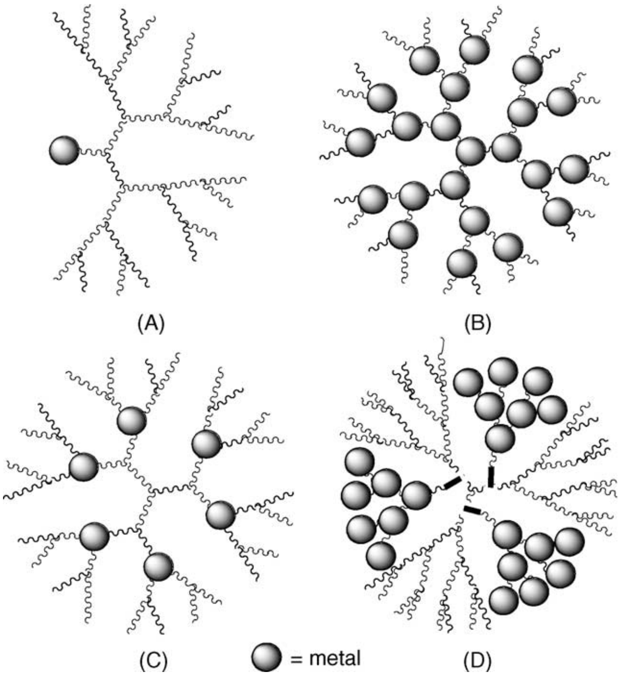
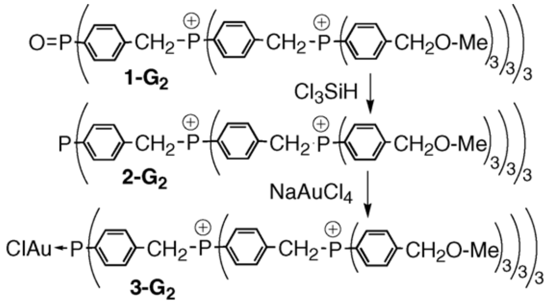


Fig. 1. Possible location of metallic groups inside dendrimers.



Scheme 1.

Most metallodendrimers are built from organic skeletons, in particular from dendrimers of types polyamidoamine (PAMAM) [5], polybenzylether [6], or polypropyleneimine [7]. However, a lot of examples are also known for heteroatom-containing dendrimers [8], and particularly for phosphorus-containing dendrimers [9]. The purpose of this paper is to review the metallodendrimers of types A–D built from phosphorus-containing dendrimers that are dendrimers possessing phosphorus at each branching point. The first part of this review will concern the synthetic aspect, and the second part will describe the properties and applications of these metallo-phosphorus dendrimers, mainly in the field of catalysis. Indeed, these compounds should possess the advantages of classical homogeneous catalysis in terms of activity and selectivity, and in addition their size should facilitate the catalyst–product separation, which is usually non-trivial. This point is of crucial importance for pharmaceutical industry or when the metal catalysts and ligands are expensive.

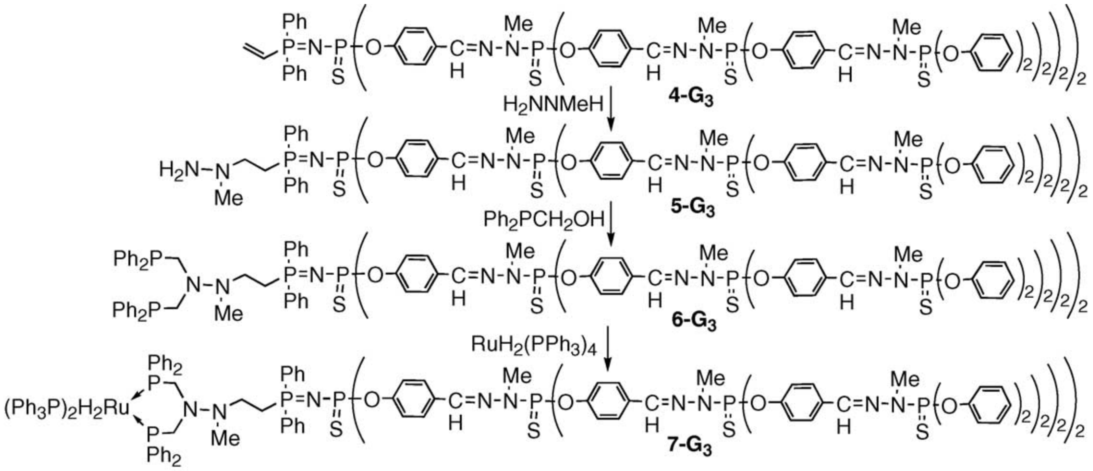
2. Syntheses of metallo-phosphorus dendrimers

2.1. Metal only at the core (structures of type A)

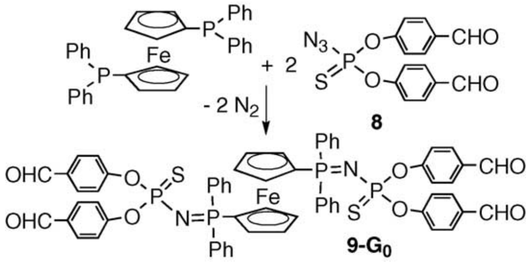
The first example of metallo-phosphorus dendrimers ever synthesized was described by Engel et al. in 1993. It possesses one gold atom complexed by a phosphine located at the core, and it was obtained by reduction of the phosphine oxide core of **1-G$_2$**, which affords the free phosphine **2-G$_2$** (Scheme 1) [10].

We have synthesized another example of type A compounds, in which the metal is complexed by a diphosphine. The precursor is the dendron **4-G$_3$** possessing a vinyl group at the core [11]. This compound undergoes first a Michael type addition of methylhydrazine, followed by the condensation of 2 eq. of Ph_2PCH_2OH. This reaction affords the diphosphine **6-G$_3$**, which is able to complex transition metal derivatives such as ruthenium hydride (Scheme 2) [12].

Ferrocene derivatives have also been used as metallic cores of dendrimers. In this case, the metallic group is not



Scheme 2.

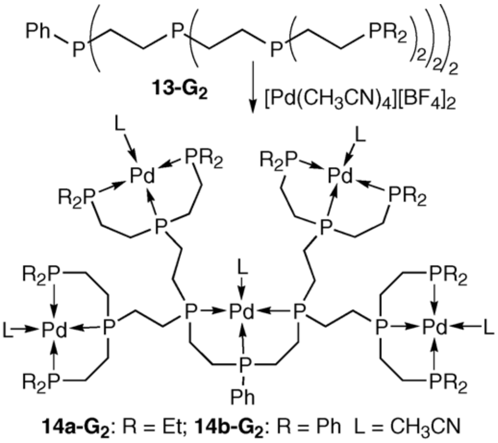


Scheme 3.

grafted at the last step of the synthesis but it is present since the very beginning. We have synthesized the generation zero of compound **9-G_0** by a Staudinger reaction of diphosphino ferrocene with the azide (**8**) (Scheme 3) [13], but also the fourth generation of the dendrimers **11-G_n** starting from ferrocene carbaldehyde (Scheme 4) [14]. The synthesis is carried out by applying our classical two-steps method [15], using alternately the phosphorhydrazide (**10**) and the sodium salt of 4-hydroxybenzaldehyde (**12**). Both steps were repeated up the obtaining of **11-G'_4**, but the synthesis could have been pursued up to higher generations. Ten dendrimers having one ferrocene as core were synthesized in this way.

2.2. Metals throughout the structure (structures of type B)

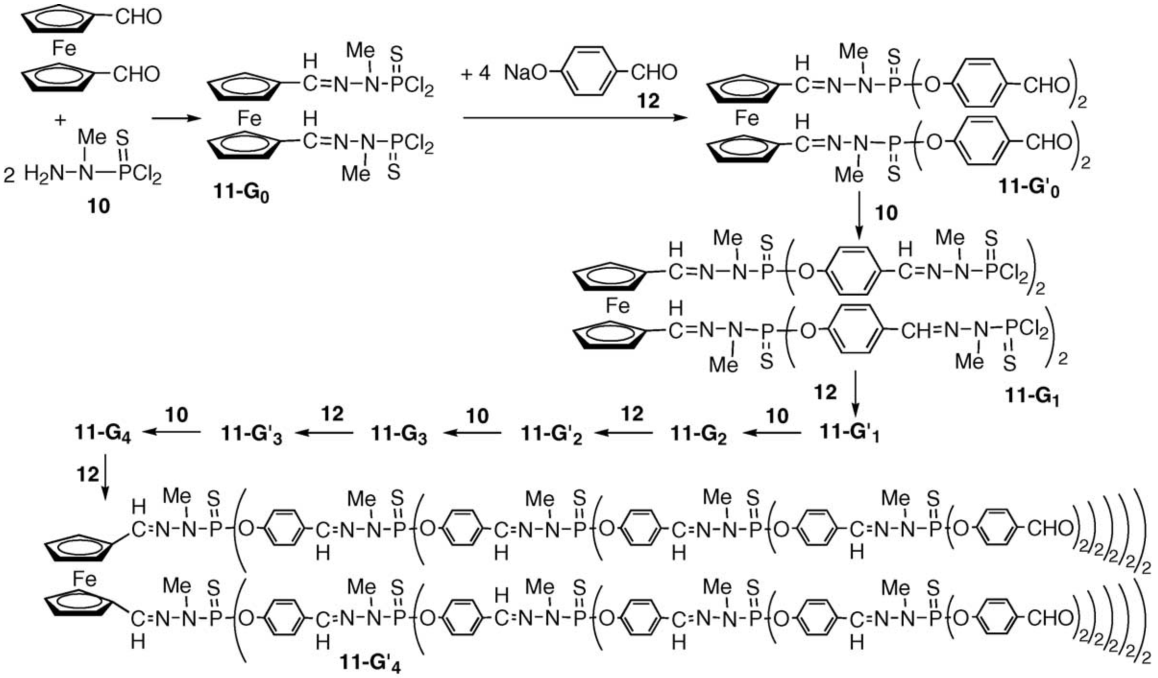
A few examples of dendrimers constituted of phosphine complexes at each branching point are known. The first compound in this series was obtained by DuBois et al., by complexation of palladium by the dendrimer **13-G_2**, which possesses 15 phosphines (Scheme 5) [16].



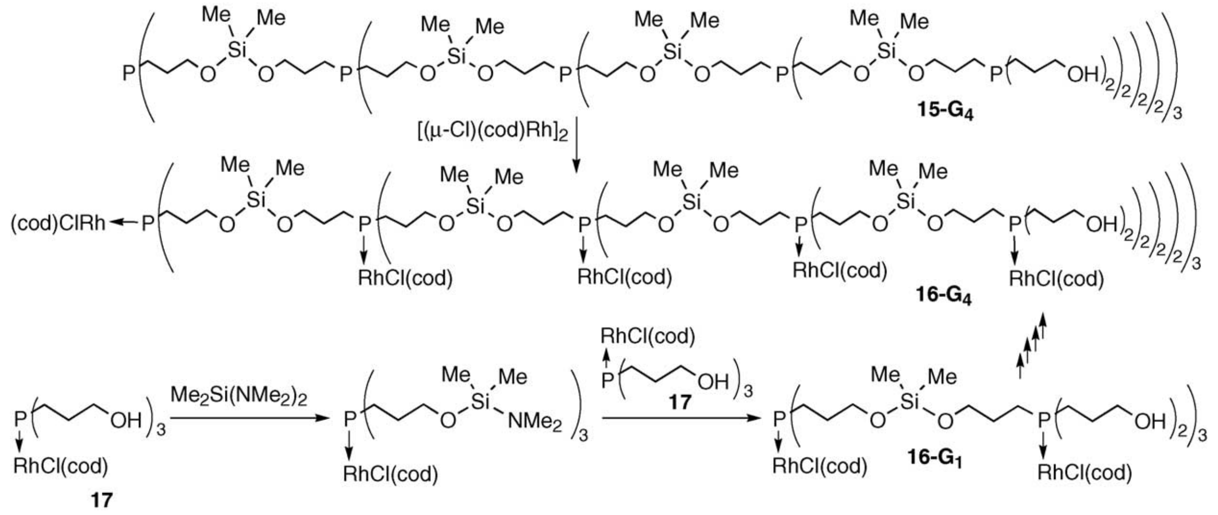
Scheme 5.

Larger complexes were obtained by Kakkar et al. from dendrimer **15-G_4** constituted of siloxane linkages between phosphines. Complexation of rhodium affords the dendrimer complex **16-G_4**; the same compound was obtained by using the phosphine complex **17** during the synthesis of the dendrimer instead of the corresponding free phosphine (Scheme 6) [17].

Recently, the same type of complexation was carried out by Salamonczyk et al. with the phosphine dendrimers **19-G_n** ($n = 2$–4) obtained after the deprotection by DABCO of the phosphino-borane dendrimers **18-G_n** (Scheme 7). A complexation reaction of **19-G_n** was also attempted with $Pd(cod)Cl_2$. No phosphine remains free; five palladium



Scheme 4.

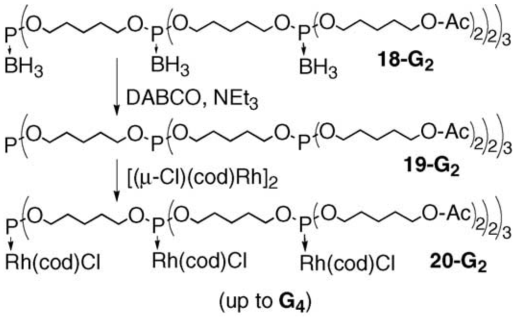


Scheme 6.

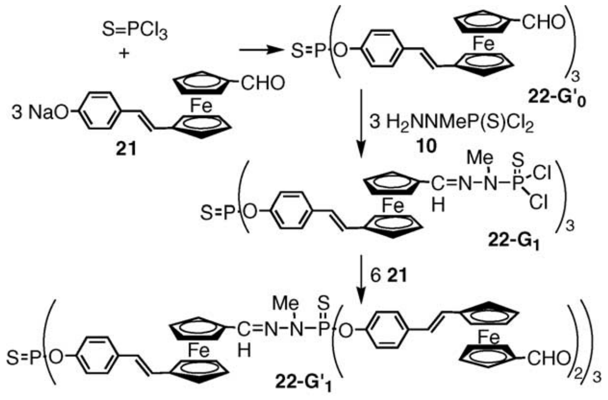
derivatives were complexed, each by two phosphines, but a statistical distribution of the metals is observed [18].

Beside the complexation of phosphines, which occurs at the branching points, metallic groups can be included within the linkages constituting the branches. In this field, we have particularly studied the case of ferrocene derivatives. In order to be consistent with our classical way of synthesis of dendrimers [15], these ferrocenes must possess both an aldehyde and a phenol group, as illustrated for instance by the ferrocene derivative **21**. Its reaction with $P(S)Cl_3$ affords the generation zero of dendrimer **22-G**$'_{n}$. The synthesis was pursued using the phosphorhydrazide (**10**), then again the ferrocene (**21**), to afford finally dendrimer **22-G**$'_{1}$, possessing two layers of ferrocenes (Scheme 8) [19].

A larger dendrimer possessing three layers of ferrocenes was obtained using the ferrocene derivative **23**, which possesses also an aldehyde and a phenol group. Applying a method of synthesis analogous to the one shown in Scheme 8, the second generation **24-G**$'_{2}$ was obtained (Scheme 9) [14]. The only difference between both series of dendrimers concerns the presence or not of a CH=CH linkage between the ferrocene and the phenol.



Scheme 7.

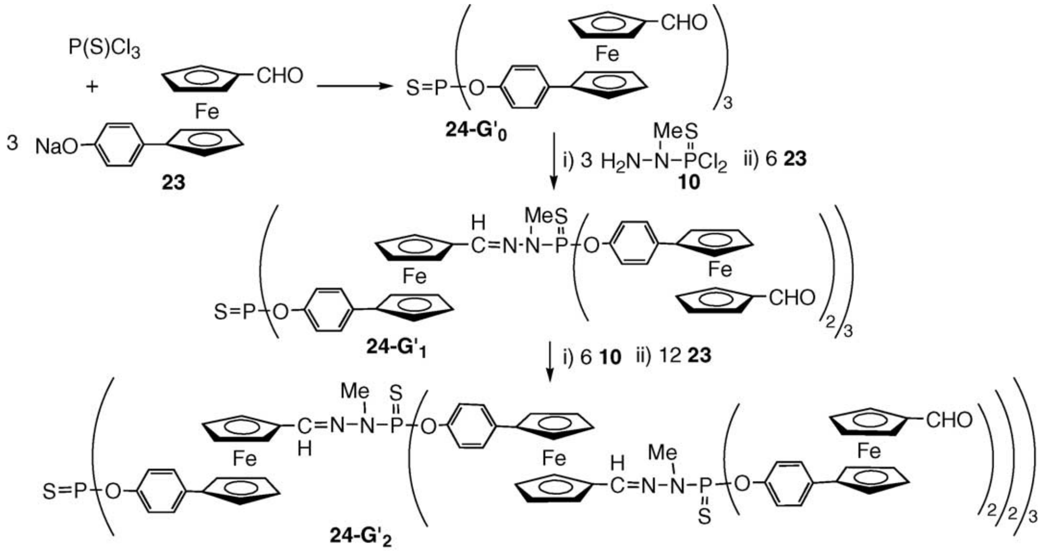


Scheme 8.

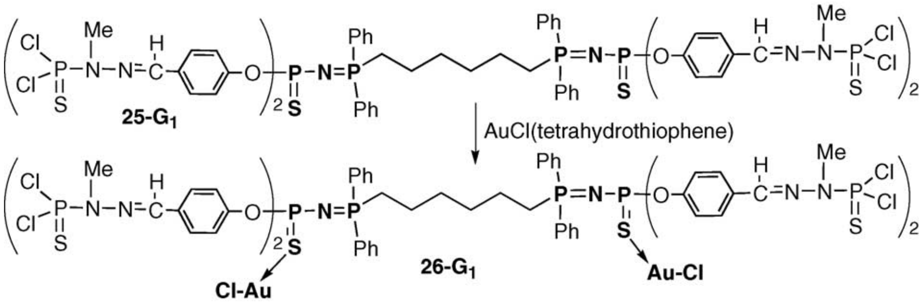
2.3. *Metals at one or several specific layers, "layer-block dendrimers" (structures of type C)*

The presence of metals only at selected layers necessitates the synthesis of layer-block [20] dendrimers that are dendrimers constituted of two (or more) types of branches, depending on the level of their location inside the structure. All the examples concerning phosphorus dendrimer complexes in this particular field come from our group. As shown in the previous examples, here also the metal can be linked to (selected) branching points or within (selected) linkages of branches.

Examples concerning the complexation at some branching points take profit of the presence of P=N–P=S linkages [21], obtained by Staudinger reactions between phosphines and phosphorus azides. The sulfur atom of these linkages is able to complex gold, whereas the other P=S groups not included in P=N–P=S linkages, do not react with gold. This selective complexation has been carried out with the first generation **25-G**$_{1}$ (Scheme 10), but also with the third generation **27-G**$_{3}$ (Scheme 11) [22]. The latter case illustrates the high



Scheme 9.



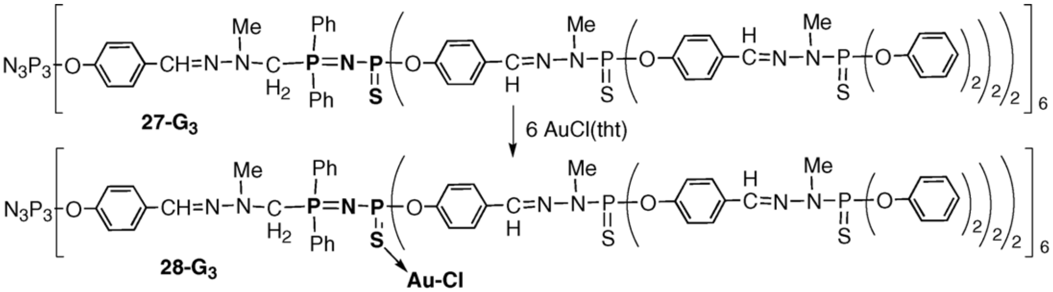
Scheme 10.

specificity of this complexation, which occurs only at the branching points of the first generation.

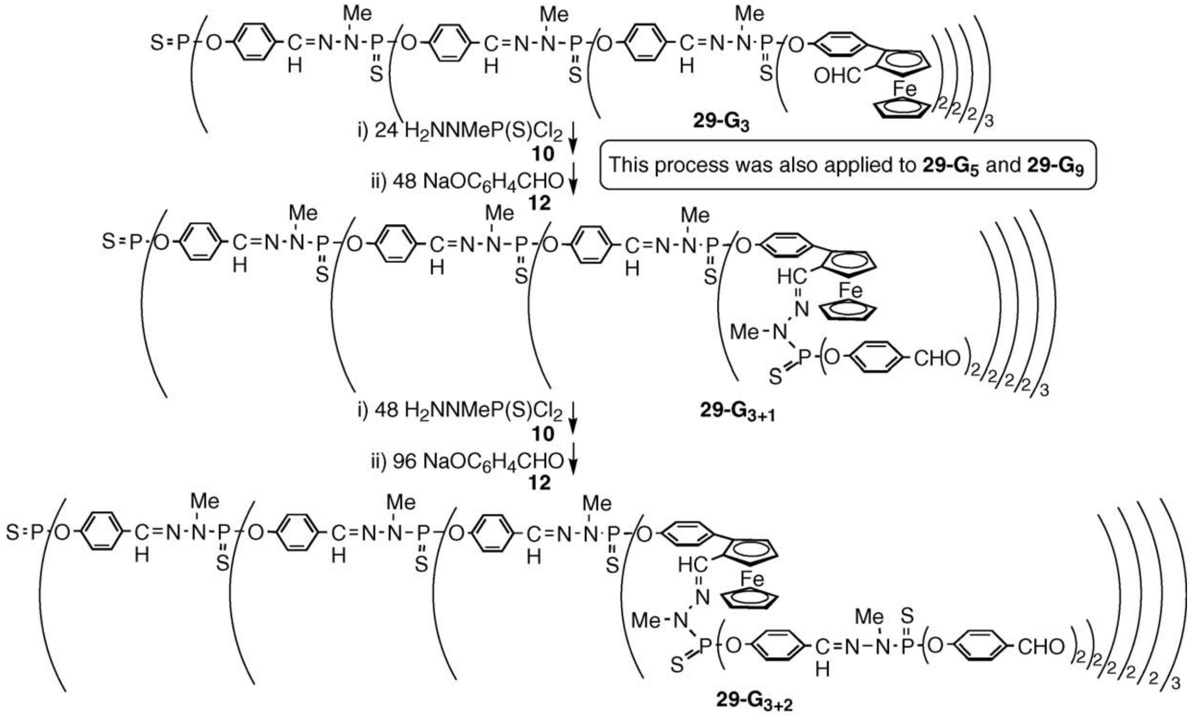
We used also a ferrocene derivative linked to an aldehyde to include metals in selected branches. The ferrocene was first grafted to the surface of a third generation dendrimer [23], then the aldehydes were reacted with the phosphorhydrazide (**10**) to continue the growing of the dendrimer, inducing a progressive burying of the layer of ferrocenes. Two generations were added to the ferrocenes layer, affording finally dendrimer **29-G$_{3+2}$** (Scheme 12) [24]. The same type of reactions was also applied to dendrimers **29-G$_5$** and **29-G$_9$**, leading to dendrimers **29-G$_{5+2}$** and **29-G$_{9+2}$**, respectively.

2.4. *Metals in selected branches, "segment-block dendrimers" (structures of type D)*

Such a type of complex is obtainable only for dendrimers having some branches whose chemical composition is different from the other ones, and are called "segment-block dendrimers" [20]. They could be obtained by grafting two types of dendrons to a core, but in fact the only examples known up to now for phosphorus-containing dendrimers are built by growing step-by-step new branches inside a dendrimer. Such reaction take profit of the presence of P=N–P=S linkages where wanted, which can be desulfurized and reacted



Scheme 11.

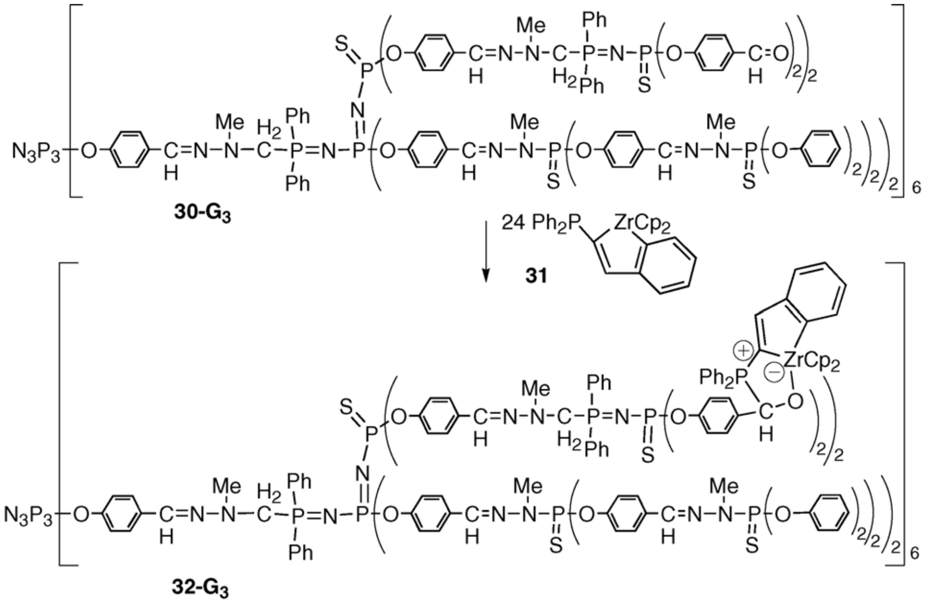


Scheme 12.

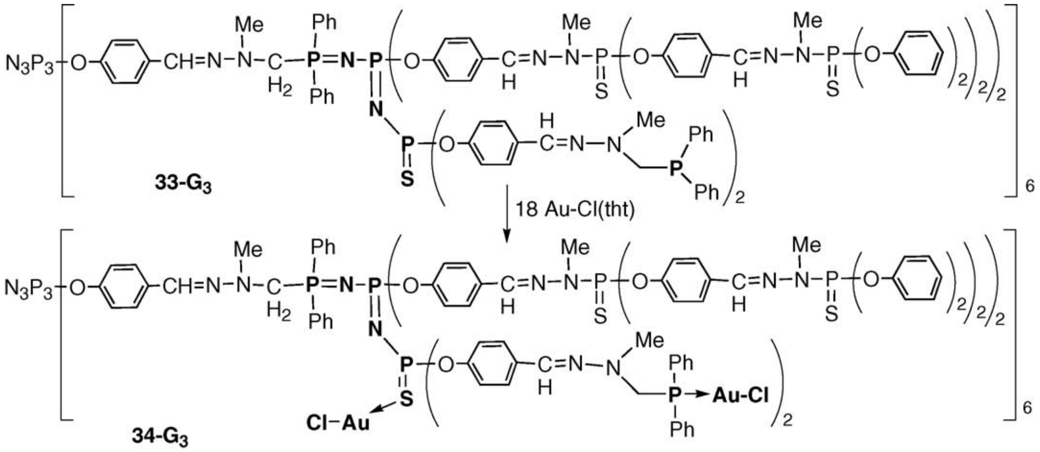
with azides [25]. Compound **30-G$_3$** was synthesized in this way. Its aldehyde groups located on the periphery of some internal branches undergo formal [3 + 2] cycloaddition reactions with 2-phosphino-1-zirconaindene (**31**). These reactions lead to unusually stable anionic zirconocene complexes inside dendrimer **32-G$_3$**, which constitute the first example of polyzwitterionic metallodendrimers (Scheme 13) [26].

The reactivity of the P=N–P=S linkages has been used also for the internal grafting of phosphines, affording dendrimer **33-G$_3$**, which possesses two types of potentially complexing groups: the phosphines and the sulfur atom of the P=N–P=N–P=S linkages. Complexation of gold occurs as expected on both types of complexing sites, affording compound **34-G$_3$**, in which two layers of the internal branches are complexed (Scheme 14) [22].

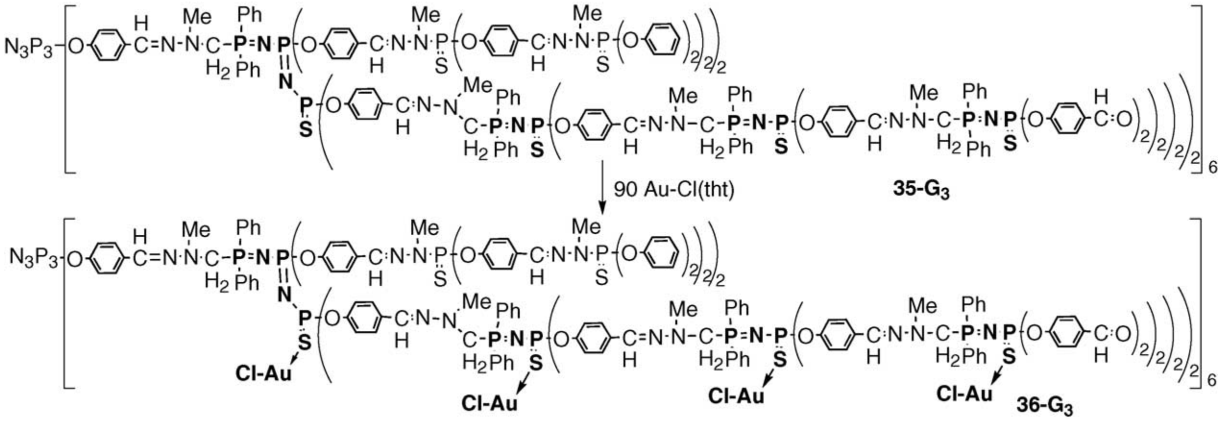
The largest compound in this field is obtained by the step by step growing of new branches inside the “parent” dendrimer; these new branches have a chemical composition



Scheme 13.



Scheme 14.



Scheme 15.

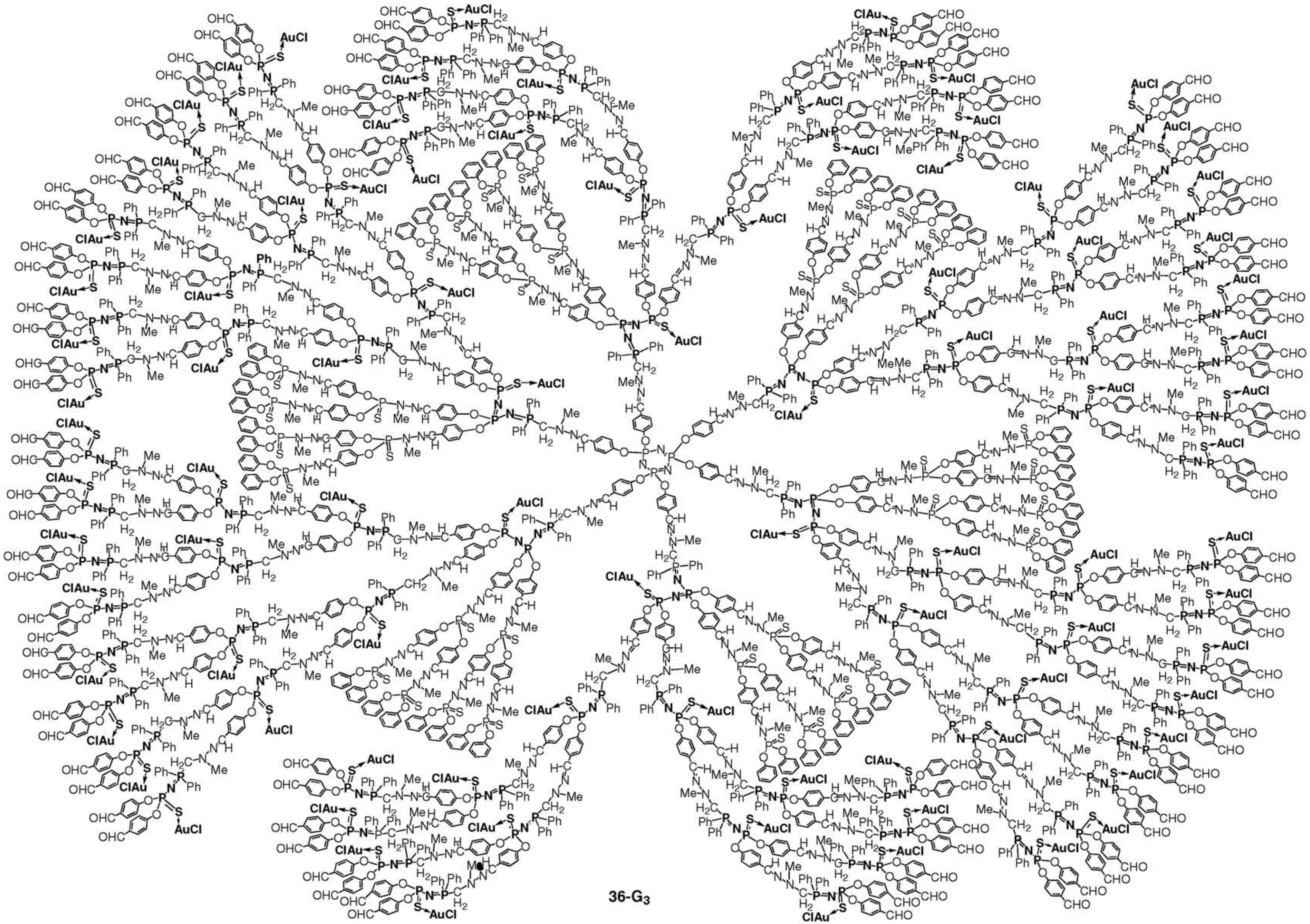
different from that of the “parent” branches. In particular, these new branches include P═N─P═S linkages, which are able to complex gold, as emphasized previously. Thus, the reaction of dendrimer **35-G$_3$** with 90 eq. of gold affords the complex **36-G$_3$** (Scheme 15) [22]. Only the four layers including P═N─P═S linkages are able to complex gold, whereas the other P═S groups do not react (Fig. 2).

3. Properties

The presence of metals offers the very unique opportunity to study the influence of the relative “burying” of a functional group inside a dendrimer. Ferrocene derivatives are particularly useful as sensors for this purpose. Electrochemical studies of dendrimer **22-G$'_1$** show that the ferrocenes of the inner and outer layers can be differentiated (Fig. 3) [19]. The difference of potential observed between both layers is due to the presence of the strong electron-withdrawing formyl groups, which induce a higher oxidation potential for the outer layer. Surprisingly, oxidation of the inner layer induces drastic changes in the solubility, which leads to the deposition of this dendrimer on the Pt working electrode. Such behavior is in marked contrast with the general observation that solubility is mainly governed by the end groups, and might be an indication of the back-folding of the external branches, which would expose the inner layers to the exterior.

Only two waves are also observed on the cyclic voltammogram of the dendrimer **24-G$'_2$** having three layers of ferrocenes; the one at high potential corresponds to the outer layer, and the other one corresponds to both inner layers [14].

Study of the behavior of the series **29-G$_n$–29-G$_{n+2}$** affords new insights on the influence of the location of functional groups inside a dendrimer on the property considered. Electrochemical studies carried out with this series show the expected decrease of the oxidation potential on going from **29-G$_n$** to **29-G$_{n+1}$**, due to the replacement of aldehydes by hydrazones. Two additional phenomena have to be noted: first, the rate of the electronic transfer decreases when the ferrocenes are more confined within the dendrimer; second, the reversibility of the system decreases with the increase of the generation of the dendrimer within the same series, as illustrated for the **29-G$_5$** series in Fig. 4. Furthermore, if the initial dendrimer is large, the irreversibility of the oxidation is more pronounced when adding a first, then a second layer [24].



36-G₃

Fig. 2. Chemical structure of a segment block dendrimer, showing the specific complexation of gold by layers including P═N─P═S linkages.

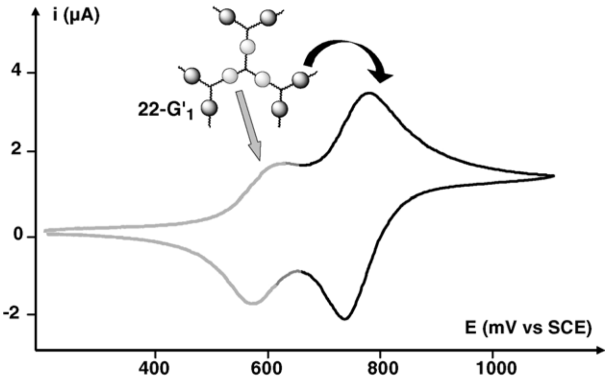


Fig. 3. Cyclic voltammogram showing two different layers of ferrocenes in dendrimer **22-G′$_1$** (adapted from Ref. [19]).

An analogous behavior is also observed for the series **11-G′$_n$**, in which a single ferrocene is located at the core: the cyclic voltammogram of the first generation shows a good reversibility, whereas a pronounced irreversibility is observed for the second generation [14]. In both cases, no influence of the oxidation on the solubility is observed when the ferrocenes are surrounded by at least one layer of branches, contrary to what was observed for **22-G′$_1$**.

Thus, electrochemistry furnishes interesting information about the steric accessibility to these ferrocenes. Furthermore, the ferrocenes included in dendrimers **29-G$_{n+x}$** are chiral (planar chirality), and study of their chiroptical properties should give information about conformational order inside these dendrimers. The chemical environment of the chiral groups has a dramatic influence on the molar rotation $[\alpha]_{\text{mol}}$, on going from **29-G$_n$** to **29-G$_{n+1}$**, whereas practically no modification is observed on going from **29-G$_{n+1}$** to **29-G$_{n+2}$**, as shown in Fig. 5 for the value of the molar rotation divided by the number of chiral units. Furthermore, this value is a constant for each series **29-G$_3$**–**29-G$_9$**, or **29-G$_{3+1}$**–**29-G$_{9+1}$**, or **29-G$_{3+2}$**–**29-G$_{9+2}$** [24]. Thus, the relative burying of the chiral shell within the interior of these dendrimers has no influence upon their chiroptical properties, contrarily to what was observed for the electrochemical properties of the same dendrimers.

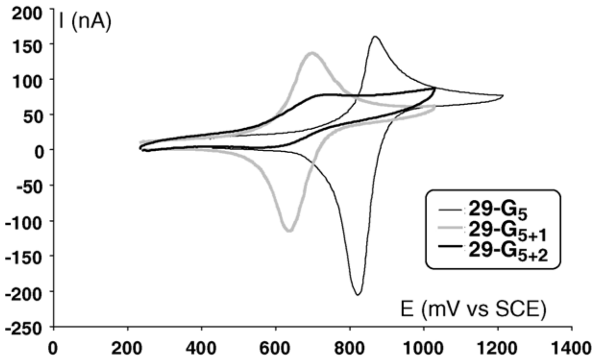


Fig. 4. Cyclic voltammograms showing the influence of the progressive "burying" of the ferrocene layer inside dendrimer **29-G$_5$** (adapted from Ref. [24]).

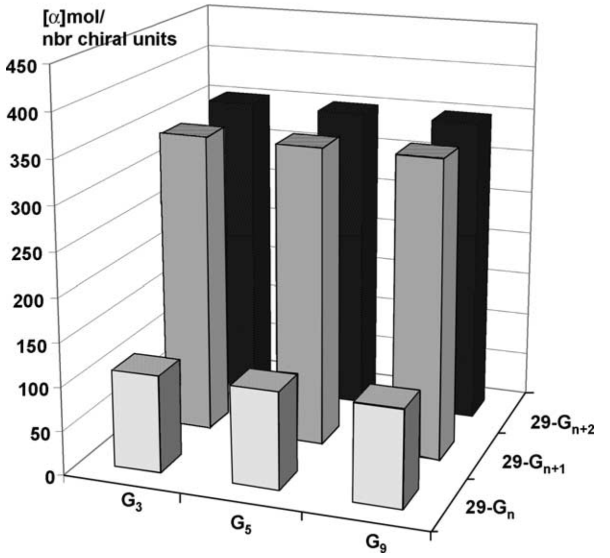


Fig. 5. Molar rotation divided by the number of stereogenic groups vs. generations (adapted from Ref. [24]).

4. Applications in catalysis

Some of the complexes shown in the previous sections were synthesized with the aim of using them as catalysts. The idea was to combine both the advantages of homogeneous catalysis because dendrimers are soluble, and the advantages of heterogeneous catalysis because dendrimers can be easily recovered and reused, due to their large size. Such application was recognized very early, as shown by the use of complexes **14a**,**b-G$_2$** as catalysts for the electrochemical reduction of CO_2 to CO in 1994. The efficiency of the catalyst was found very similar to that of analogous monomeric catalysts [16].

The second example of catalysis concerns also dendrimers having metals throughout their structure. Indeed, the series **16-G$_n$** ($n = 0$–4) was used as catalyst of the hydrogenation of decene, in a 1:200 metal-to-substrate ratio. Whatever the generation is, the catalytic activity was found similar to that of the corresponding monomeric complex, in terms of turnover number ($\text{mol}_{\text{prod}}/\text{mol}_{\text{cat}} = 200$) and turnover frequency ($\text{mol}_{\text{prod}}/\text{mol}_{\text{cat}}/\text{h} = 400$). The fourth generation **16-G$_4$** was recovered and reused one time: the catalyst was found still active, with only a 5% decrease of the conversion of decene [17].

Finally, the last example of catalysis using phosphorus dendrimers having metals inside their structure concerns dendrimer **7-G$_3$**, in which a single metallic center is located at the core. We have carried out the experiment in comparison with a dendrimer possessing the same metallic groups on the whole surface. We have shown that both types of dendrimers are equally efficient for the diastereoselective Michael addition involving ethylcyanoacetate and diethyl ethylidene malonate, and that dendrimer **7-G$_3$** does not exhibit higher substrate selectivity. This dendrimer can be recycled and reused three times without loss of activity [12].

5. Conclusion

This review has emphasized the structural diversity of phosphorus dendrimers possessing metallic derivatives somewhere in their internal structure (core or branches). Beside the synthetic challenges and the pleasant aesthetic of these compounds, metals placed where desired inside the structure have been used in some cases as sensors to study the influence of the location of a functional group on its properties. In other cases, the metallic groups were used as catalysts; generally no differences are detected between the efficiency of the dendritic catalyst and of the corresponding monomer. However, the dendritic catalysts possess the advantage to be recovered and reused with a very good efficiency, contrarily to the corresponding monomers. These are the sole uses of metallo-phosphorus dendrimers up to now, thus more work is needed to expand the applications of such compounds. However, in view of the number of properties already described for metallo-organic dendrimers such as magnetic, electronic, or photo-optical properties, one may anticipate that metallo-phosphorus dendrimers, particularly those having conjugated linkages, might afford compounds with enhanced efficiencies in these fields (and in others).

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