Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 1928–1939
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Decorating step-by-step and independently the surface and the core of dendrons

Inma Angurell [a,b], Cédric-Olivier Turrin [a], Régis Laurent [a], Valérie Maraval [a], Paul Servin [a], Oriol Rossell [b,*], Miquel Seco [b], Anne-Marie Caminade [a,*], Jean-Pierre Majoral [a,*]

[a] Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex 4, France
[b] Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

Received 27 November 2006; received in revised form 4 January 2007; accepted 5 January 2007
Available online 13 January 2007

Abstract

Dendrons possessing one activated vinyl group at the core and several chlorine atoms at the end of the branches are used as starting materials to study the possibility to react independently the surface functions and the core function. In particular, the most powerful sequence of reactions for decorating them by organometallic complexes as end groups and amine or alcohol at the core has been determined. In the first step, phenol phosphines are grafted as end groups of the dendrons, and they can be used for the complexation of metals. However, these phosphines must be kept free when amines are used to react with the vinyl core in the next step. Depending on the type of phosphine end groups and on the type of function of the core (amine or alcohol), the complexation of ruthenium ($[RuCl_2(p\text{-cymene})]_2$) and rhodium ($[RhCl(COD)]_2$) derivatives by the phosphine end groups can occur without side reaction at the core.

Keywords: Dendrons; Dendrimers; Phosphines; Complexes; Ruthenium; Rhodium

1. Introduction

Dendrons [1] also called dendritic wedges [2], are nanometric trees constituted of numerous branches linked to a trunk (the core). Compared to dendrimers [3,4], this versatile class of dendritic molecules possesses the advantage to have functional groups (generally different) both at the level of the core and at the end of the branches. Such feature is particularly interesting to elaborate special and complex dendritic architectures [5–7]. However, this advantage is often more theoretical than practical, due to the necessity for one type of these functions to be non reactive during the synthetic process; either the functions located at the surface for dendrons built by a convergent process, or the function located at the core for dendrons built by a divergent process must be insensitive to the conditions used for the growing [5]. Furthermore, this/these "non reactive" functional group(s) must be able to react after the synthesis of the dendron.

We have already described the synthesis of phosphorus-containing dendrons possessing an activated vinyl group at the core [8], and we have shown that this vinyl group can easily react with primary and secondary amines, provide the end groups are poorly reactive functions, such as a nitrile or an aromatic tertiary amine [9]. The sole example in this series in which the core and the surface react is when the end groups are aldehydes; in this case, both functions react with hydrazines, thus they are not useful because they finally afford the same type of functions at both levels [8]. We report here the original strategy to react independently the functions located on the surface and the function located at the core of dendrons, and the possibility to graft new functional and reactive groups by this way.

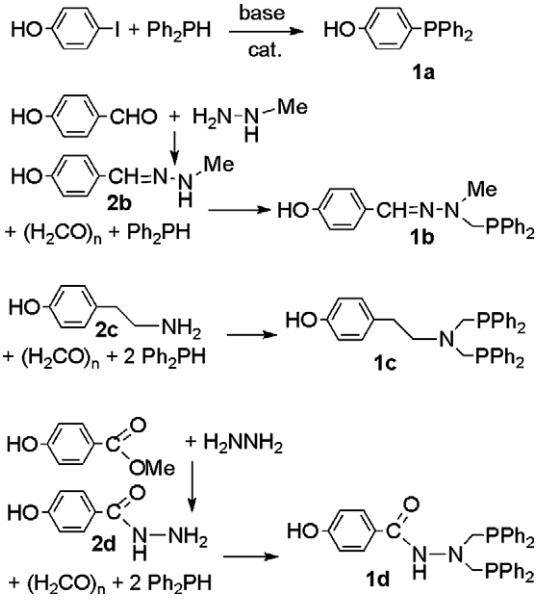
* Corresponding authors. Tel.: +33 561 33 3125; fax: +33 561 55 3003 (A.-M. Caminade, J.-P. Majoral).
E-mail addresses: oriol.rossell@qi.ub.es (O. Rossell), caminade@lcc-toulouse.fr (A.-M. Caminade), majoral@lcc-toulouse.fr (J.-P. Majoral).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.01.001

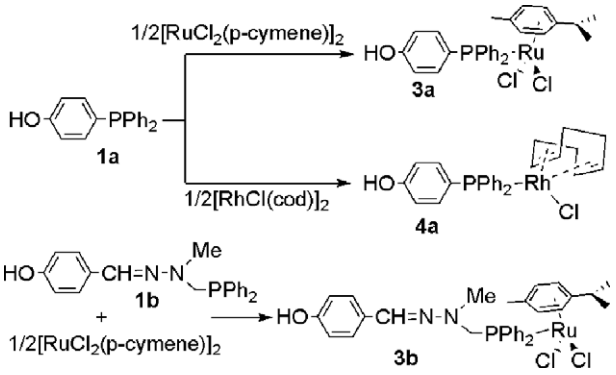
2. Results and discussion

Amongst the various areas of researches about dendritic molecules, one of the most active concerns organometallic chemistry [10,11], often carried out with the aim of using the resulting complexes as catalysts [10–16]. We reasoned that dendrons possessing organometallic derivatives as end groups and one reactive functional group at the core would be valuable targets. One of the easiest way to obtain metallic complexes consists in using phosphines, thus our first aim was to graft phosphines as end groups of dendrons. For this purpose, we synthesized first a series of phenol phosphines **1a-d**; the OH group was chosen to allow the grafting on the $P(S)Cl_2$ end groups of dendrons. The synthesis of the monophosphine **1a** was previously described [17]; monophosphine **1b** and diphosphines **1c** and **1d** are synthesized by a Mannich-type reaction between Ph_2PCH_2OH, generated in situ from Ph_2PH and paraformaldehyde, and NH or NH_2 functions of phenols **2b**, **2c** and **2d** (Scheme 1).

The complexation ability of the monophosphines, considered as model compounds, was tested in order to determine the most convenient conditions of reactions and the influence of the complexation on the NMR spectra. We choose ruthenium and rhodium as metals to be complexed, in view of their known ability to generate active catalytic species [18]. In all cases, 1/2 equivalent of the metallic dimer $[RuCl_2(p\text{-cymene})]_2$ or $[RhCl(cod)]_2$ per phosphine is used (Scheme 2). Obviously, ^{31}P NMR is the most informative tool to ascertain the complexation; an important deshielding of the signal corresponding to the phosphine is observed upon complexation ($\Delta\delta^{31}P = +24$ ppm for **1a** → **3a**; +38 ppm for **1a** → **4a**; +42 ppm for **1b** → **3b**). In the case of complex **4a**, a doublet with a characteristic $^1J_{PRh}$ coupling constant (149 Hz) is observed. It must be noted that in the three cases, the presence of phenol is compatible with the presence of Cl on the metal.



Scheme 1.

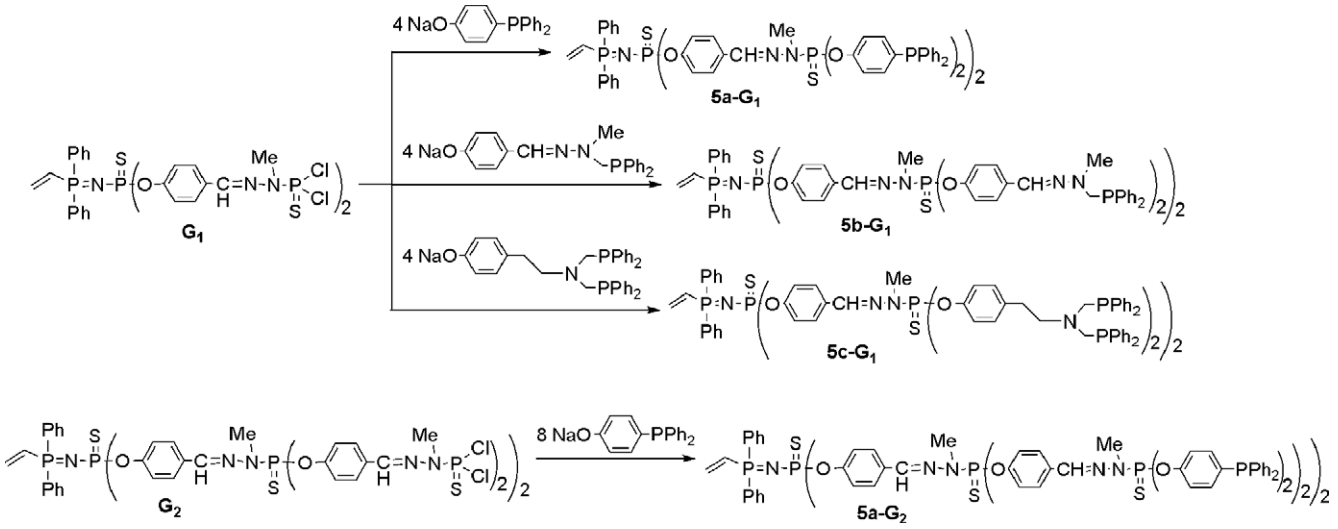


Scheme 2.

However, we did not succeed when trying to graft these complexes in basic conditions on the $P(S)Cl_2$ end groups of the first generation dendron $\mathbf{G_1}$, which possesses four chlorine on the surface and one activated vinyl group at the core [8]. This dendron will be our starting material for testing the possibility to decorate independently and successively the surface and the core with other functional groups. We have already shown that the vinyl group at the core is able to undergo the addition of primary or secondary amines [8], but this reaction is not compatible with the presence of the $P(S)Cl_2$ end groups, which also react easily with amines [19,20]. Thus, the first step to decorate this dendron must concern the reactivity of the end groups.

The grafting of the free phosphines **1a-d** as end groups of dendron $\mathbf{G_1}$ was successfully attempted, using their sodium salts generated by reaction with NaH. The reactions proceed completely overnight for the monophosphines **1a** and **1b**, and after one day for the diphosphine **1c**, to afford dendrons **5a-G$_1$**, **5b-G$_1$**, and **5c-G$_1$**, respectively (Scheme 3). Monitoring these reactions by ^{31}P NMR shows first the disappearance of the signal corresponding to the $P(S)Cl_2$ end groups ($\delta^{31}P = 63.5$ ppm) on behalf of the appearance of a new singlet corresponding to the monosubstitution (P(S)ClOAr), for instance at $\delta^{31}P = 72.3$ ppm for the reaction with **1c**. This intermediate signal totally disappears when the substitution is complete, as shown by the appearance of a singlet at 66 ppm for the $P(S)(OAr)_2$ groups. Obviously the signal of the mono- or di-phosphine end groups is also detected ($\delta^{31}P = -3.1$ ppm for **5a-G$_1$**, −19.7 for **5b-G$_1$**, −25.1 for **5c-G$_1$**), as well as two doublets corresponding to the P═N─P═S linkage.

^{31}P NMR ascertains the purity of these dendrons with a precision better than 1%, but it also showed that the reaction between **1d** and $\mathbf{G_1}$ did not afford a pure compound. The signals corresponding to the expected **5d-G$_1$** dendron are observed (two doublets at $\delta^{31}P = 15.1$ and 56.3 ppm with $^2J_{PP} = 32$ Hz for the P═N─P═S linkage of the core, and two singlets at 65.4 and −22.7 ppm for the P(S) and phosphine terminal groups, respectively). However, dendron **5d-G$_1$** is accompanied by impurities impossible to

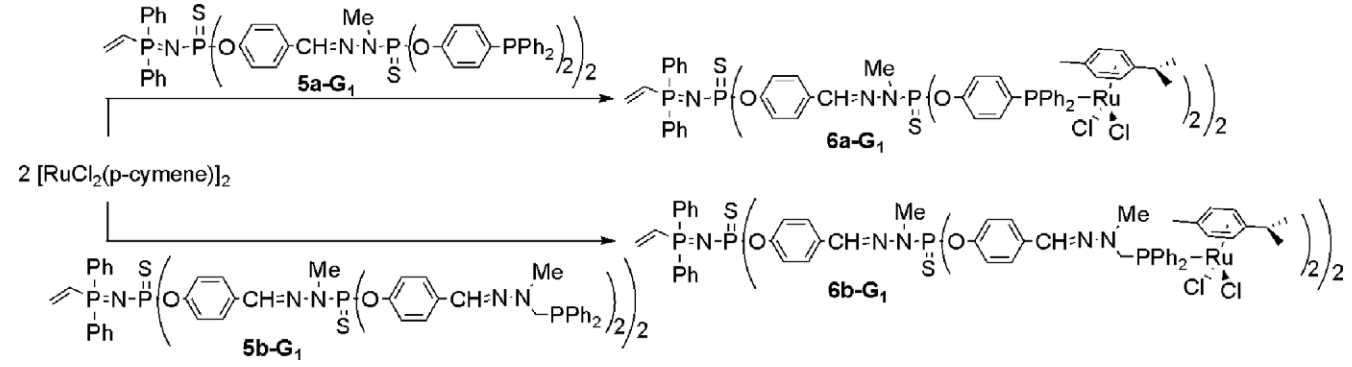


Scheme 3.

eliminate, which might be due to the presence of a N–H bond (absent in all the other compounds), thus no more attempt to use diphosphine **1d** was carried out. On the other hand, in order to demonstrate that the grafting of phosphines is not limited to the first generation dendron, the sodium salt of **1a** was also reacted with the second generation dendron $\mathbf{G_2}$ (Scheme 3). The expected dendron **5a-$\mathbf{G_2}$** bearing 8 phosphine end groups is easily isolated and characterized as previously by multinucleus NMR, and particularly by ^{31}P NMR. The ^{31}P NMR spectrum displays exclusively the expected signals (two doublets at 14.0 and 56.5 ppm with $^{2}J_{PP} = 31.9$ Hz for the P═N─P═S linkage of the core, and 3 singlets at −2.9 for the phosphine end groups, 65.2 for the P(S) groups of the second layer, and 65.9 for the P(S) groups of the first layer).

Having in hand this series of dendrons functionalized by an activated vinyl group at the core and decorated by 4 or 8 phosphines as end groups, we decided to study the reactivity of both sites. In a first attempt, we decided to use again the reactivity of the surface, and in particular to complex ruthenium derivatives. The reaction of two equivalents of $[RuCl_2(p\text{-cymene})]_2$ with one equivalent of dendrons **5a-$\mathbf{G_1}$** and **5b-$\mathbf{G_1}$** occurs easily to afford the expected dendron complexes **6a-$\mathbf{G_1}$** and **6b-$\mathbf{G_1}$**, respectively (Scheme 4). The important deshielding effect observed upon complexation ($\Delta\delta^{31}P = +30$ ppm for **5a** → **6a**; + 49 ppm for **5b** → **6b**) is comparable to that observed for the model complexes **3a** and **3b**. It must be noted that no reaction occurs at the level of the core, despite the presence of the vinyl group, as shown both by ^{31}P NMR (no change for the proximate P═N─P═S linkage) and by ^{1}H NMR (no change for the vinyl group). We also attempted to react 4 equivalents of $[RuCl_2(p\text{-cymene})]_2$ with one equivalent of dendron **5c-$\mathbf{G_1}$**, but the ^{31}P NMR spectrum demonstrates that the complexation did not occur cleanly, presumably due to the difficulty to accommodate two metallic fragments in close proximity [21].

Starting from the dendron complexes **6a-$\mathbf{G_1}$** and **6b-$\mathbf{G_1}$**, we attempted to react ethylenediamine to their vinyl core, in order to have a primary amine, which is a highly versatile function. We have already shown that primary and secondary amines react by Michael-type additions to activated vinyl groups [8,9]; however, when the reaction is carried out with a diamine, a large excess of diamine must be used in order to avoid the connection of two dendrons together. The use of such excess has no consequence when the end



Scheme 4.

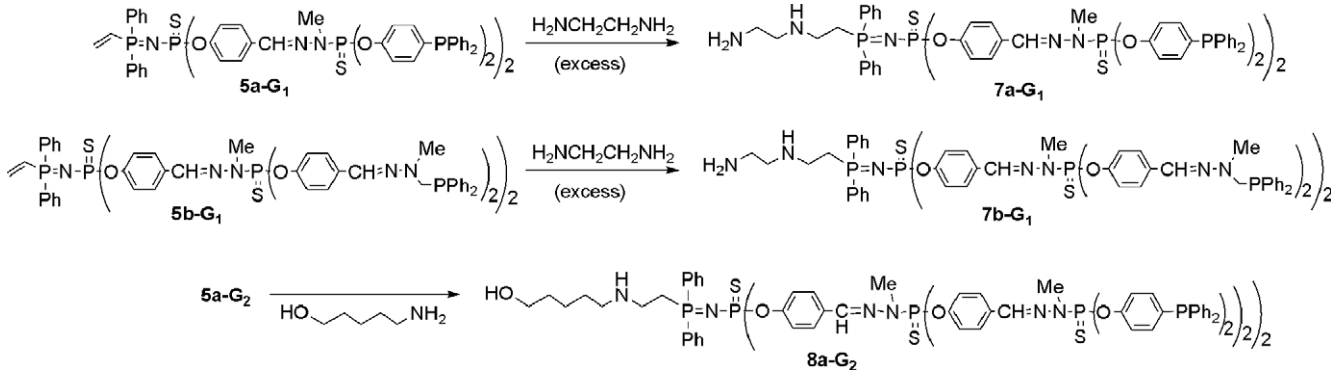
groups are non reactive, but in the case of **6a-G$_1$** and **6b-G$_1$**, we observed a degradation of the dendrons, presumably due both to a partial reaction of Ru–Cl with the diamines and the leaching of the metal (the signal of free phosphine is detected). Thus we decided to carry out the reactions at the level of the core before the complexation by the phosphine end groups.

A ten-fold excess of ethylenediamine was reacted with dendrons **5a-G$_1$** and **5b-G$_1$**. The completion of the reaction is first shown by ^{31}P NMR, which displays an important deshielding of the signal corresponding to the $Ph_2P{=}N$ group, from 14 ppm for **5a-G$_1$** and **5b-G$_1$** to 21 ppm for **7a-G$_1$** and **7b-G$_1$**. It is also shown by ^{1}H NMR, with the disappearance of the signals corresponding to the vinyl group. Furthermore, the presence of 4 different signals for the CH_2 groups in the ^{13}C NMR spectrum indicates a non symmetrical structure, corresponding to the reaction of only one side of ethylene diamine. Indeed, the reaction of both sides would give a symmetrical structure and only three signals for this fragment in the ^{13}C NMR spectrum. Thus dendrons **7a-G$_1$** and **7b-G$_1$** possess both a primary and a secondary amine at the core (Scheme 5). We have also carried out addition reactions on the second generation dendron **5a-G$_2$** with another functionalized primary amine, aminopentanol. This reaction affords dendron **8a-G$_2$** possessing both an alcohol and a secondary amine at the core (Scheme 5). The addition reaction induces the expected deshielding of the signal corresponding to $Ph_2P{=}N$ in ^{31}P NMR. It must be noted that the alcohol part of aminopentanol does not react with the vinyl group.

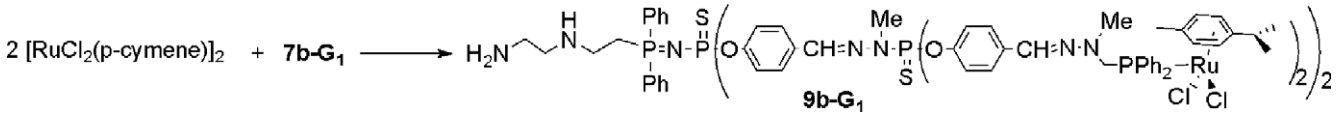
After the reactivity of the end groups illustrated by the grafting of phosphines, followed by the reactivity at the core, with the addition of various functionalized primary amines, we decided in the next step to move back to the reactivity of the end groups, by studying the complexation properties of the dendrons shown in Scheme 5. For this purpose, we tried to react $[RuCl_2(p\text{-cymene})]_2$ with dendrons **7a-G$_1$** and **7b-G$_1$**. In the case of **7a-G$_1$**, besides the reactivity of the surface, we observed a parallel reaction at the level of core. Both phenomena are easily detected by ^{31}P NMR. On one side, the spectrum displays the presence of free phosphine ($\delta = -3$ ppm) together with the complex ($\delta = 28$ ppm), which induces the occurrence of several singlets for the P(S) group of the first generation; on the other side, an important broadening of both signals of the P═N─P═S linkage indicates that ruthenium is also presumably complexed at the core. In contrast, the reaction with **7b-G$_1$** occurs rapidly and cleanly, to afford dendron **9b-G$_1$** (Scheme 6). ^{31}P NMR ascertains both the completion of the complexation by the phosphine end groups ($\delta = 29.1$ ppm) and the absence of reaction at the core. We can presume that the higher reactivity of the diphenylphosphino groups of **7b-G$_1$** compared to the triphenylphosphino groups of **7a-G$_1$** explains the absence of the side reaction at the core of **7b-G$_1$**.

In view of the problems encountered for the complexation, we decided to avoid the presence of the $NH_2CH_2CH_2NH$ linkage at the core, which might act as a chelate ligand towards the metal or substitute the chlorides, and to use the rhodium derivative, which contains only one Cl instead of two for the ruthenium derivative. We tried to react $[RhCl(cod)]_2$ with dendron **8a-G$_2$**; this reaction successfully afforded the expected complex **10a-G$_2$** after two hours at room temperature (Scheme 7). ^{31}P NMR ascertains the complete reaction of phosphines with rhodium ($\delta = 33.5$ ppm, $^1J_{PRh} = 151$ Hz), whereas the signals of the core remain unchanged.

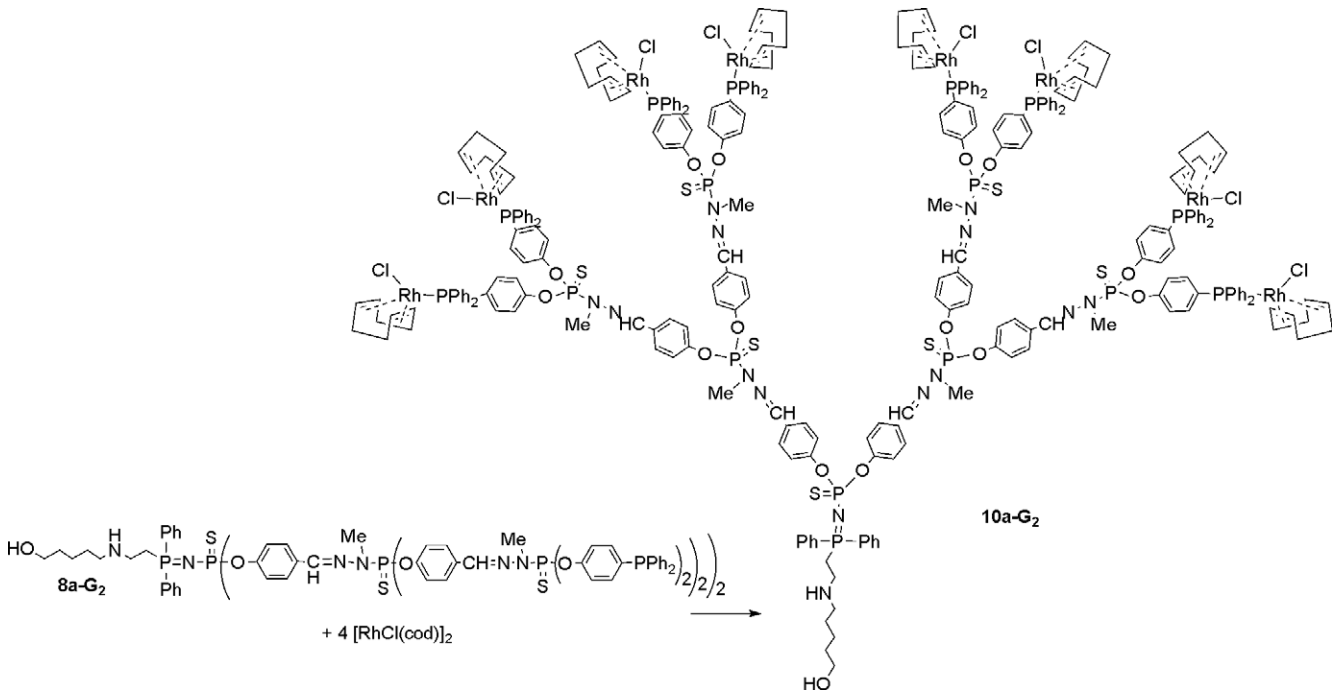
The prominent role played by ^{31}P NMR for the characterization of these dendrons has been emphasized all along this paper, and is demonstrated in Fig. 1. Indeed, all signals



Scheme 5.



Scheme 6.



Scheme 7.

corresponding to all types of phosphorus atoms are easily distinguishable, as shown for the second generation dendrons **a-G$_2$**. Each reaction induces a clear shift of the signal of the phosphorus atoms close to the place where the reaction occurs. The dotted arrows show the deshielding of the doublet corresponding to the core when the aminoalcohol is added to the vinyl group of **5a-G$_2$** (Figs. 1a and b), and the deshielding of the singlet corresponding to the phosphine end groups upon complexation of rhodium (Fig. 1b and c).

3. Conclusion

Starting from dendrons possessing one activated vinyl group at the core and 4 or 8 chlorine atoms on the surface, we have determined the most powerful sequence of reactions for decorating them by organometallic complexes. The first step concerns the grafting of phenol phosphines as end groups of the dendrons. These phosphines can be used for the complexation of metals; however such complexation precludes the use of amines to react with the core in the next step. Thus, the phosphines must be kept free when adding a primary diamine or an amino alcohol to the vinyl core. Depending on the type of phosphine end groups and on the type of function grafted to the core, we were able to complex ruthenium and rhodium derivatives by the end groups, without side reaction at the core.

Thus, we have shown ways to decorate step by step both the extremities of the branches and the "root" (the core) of these molecular "Christmas trees"-like. For the particular cases shown in this paper, the presence of amines or alcohols at the core could be useful for linking these functional dendrons to materials, whereas the presence of potentially catalytically active metal complexes could lead to catalysts possessing both the advantages of heterogeneous and homogeneous catalysis. Furthermore, it must be emphasized that such methodology is not limited to the decoration by metal complexes, and that numerous other fields can benefit from this work, such as fluorescence, biology, or nanomaterials [22] to name as a few.

4. Experimental

4.1. General

All manipulations were carried out with standard high vacuum and dry-argon techniques, due to the sensitivity of phosphines towards oxidation. The solvents were freshly dried and distilled (THF and ether over sodium/benzophenone, pentane and CH_2Cl_2 over phosphorus pentoxide, toluene over sodium). ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, DPX 300 or AMX 400 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR, $SiMe_4$ for ^{1}H and ^{13}C NMR. The attribution of ^{13}C NMR signals has been done using J_{mod}, two dimensional HMBC, and HMQC, Broad Band or CW ^{31}P decoupling experiments when necessary. The numbering used for NMR assignments is depicted in Fig. 2. The synthesis of compounds **1a** [17], **G$_1$** and **G$_2$** [8] was already described.

4.2. Synthesis of *2b*

A mixture of 4-hydroxybenzaldehyde (4.0 g, 32 mmol), and methylhydrazine (6.5 ml, 120 mmol) in absolute ethanol (50 ml) was refluxed for 5 h. After evaporation under

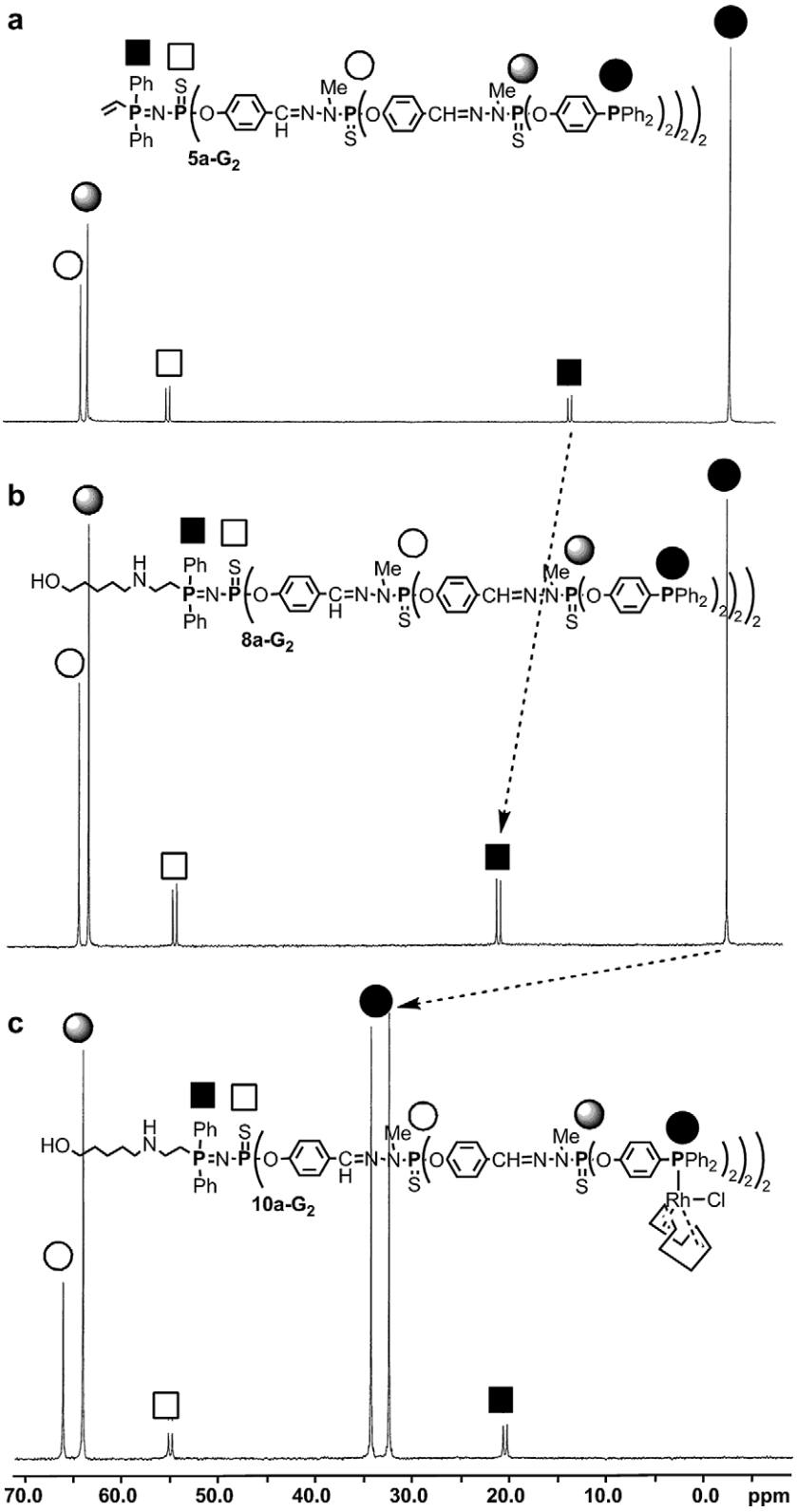


Fig. 1. ^{31}P NMR spectra (81 MHz, $CDCl_3$) of dendrons **5a-G$_2$** (a), **8a-G$_2$** (b), and **10a-G$_2$** (c).

vacuum, the residue was crystallized in hot ethyl actetate. Compound **2b** was isolated as a white powder in 81% yield.

2b. ^1H NMR (CD_3COCD_3): δ 2.87 (s, 3H, CH_3), 6.28 (br s, 1H, HN), 6.81 (d, $^3J_{HH} = 8.7$ Hz, 2H, H–C^2), 7.42 (d, $^3J_{HH} = 8.7$ Hz, 2H, H–C^3), 7.50 (s, 1H, CH=N), 8.45 (br s, 1H, OH) ppm. ^{13}C {^1H} NMR (CD_3COCD_3): δ 37.5 (s, CH_3), 118.5 (s, C^2), 130.2 (s, C^3), 132.4 (s, C^4), 137.5 (s, CH=N), 160.5 (s, C^1) ppm. Anal. Calcd for

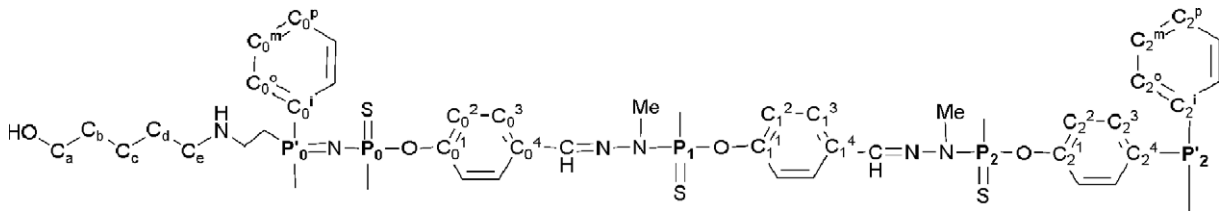


Fig. 2. Numbering used for NMR assignments.

$C_8H_{10}N_2O$ (150.2): C, 63.98; H, 6.71; N, 18.65. Found: C, 64.07; H, 6.75; N, 18.58%.

4.3. Synthesis of phosphine *1b*

A mixture of Ph_2PH (3.5 ml, 20 mmol) and paraformaldehyde (0.59 g, 19 mmol), was heated neat in a closed Schlenck tube at 120 °C for 4 h. After cooling to room temperature, THF was added, and the resulting solution was added via canula to compound **2b** (2.64 g, 18 mmol). The solution was evaporated to dryness and the resulting viscous syrup was heated overnight at 85 °C, then it was heated at 60 °C under vacuum to eliminate water. The residue was dissolved in a minimum amount of a mixture $CHCl_3$/pentane (1:1); then a powder deposited with time. This powder was washed with the same mixture of solvents, to afford **1b** as a white powder in 38% yield.

1b. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −19.8 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ 2.95 (s, 3H, CH_3), 4.17 (d, $^2J_{HP} = 2.7$ Hz, 2H, CH_2), 5.05 (br s, 1H, OH), 6.72 (d, $^3J_{HH} = 8.7$ Hz, 2H, H–C^2), 7.20 (s, 1H, CH=N), 7.27 (d, $^3J_{HH} = 8.7$ Hz, 2H, H–C^3), 7.3 (m, 6H, Ph), 7.5 (m, 4H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 39.2 (d, $^3J_{CP} = 7.7$ Hz, CH_3), 61.3 (d, $^1J_{CP} = 10.3$ Hz, CH_2), 115.3 (s, C^2), 127.2 (s, C^3), 128.4 (d, $^3J_{CP} = 6.4$ Hz, C^m), 128.6 (s, C^p), 129.7 (s, C^4), 133.0 (s, CH=N), 133.2 (d, $^2J_{CP} = 18.3$ Hz, C^o), 137.9 (d, $^1J_{CP} = 13.5$ Hz, C^i), 155.1 (s, C^1) ppm.

4.4. Synthesis of phosphine *1c*

A mixture of Ph_2PH (1.4 ml, 8 mmol) and paraformaldehyde (230 mg, 7.4 mmol) was heated neat in a closed Schlenck tube at 120 °C for 4 h. After cooling to room temperature, the reaction mixture was diluted with THF (2 ml) and added via canula to tyramine (500 mg, 3.64 mmol). The reaction mixture was degassed (freeze–thaw–pump) and heated at 85 °C overnight. The crude mixture was heated at 60 °C under vacuum to remove the volatiles. The residue was dissolved in the minimum amount of $CHCl_3$ and precipitated with a mixture of pentane and ether (1:1). The resulting powder was subjected twice to the same treatment to afford **1c** as a white powder.

1c. 45% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −24.9 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ 2.72 (t, $^3J_{HH} = 8.1$ Hz, 2H, NCH_2CH_2), 3.22 (t, $^3J_{HH} = 8.1$ Hz, 2H, NCH_2CH_2), 3.78 (br d, $^2J_{HP} = 1.8$ Hz, 4H, CH_2P), 6.5 (br s, 1H, OH), 6.80 (d, $^3J_{HH} = 8.1$ Hz, 2H, H–C^2), 6.94 (d, $^3J_{HH} = 8.1$ Hz, 2H, H–C^3), 7.4 (m, 6H, Ph), 7.5 (m, 4H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.4 (s, NCH_2CH_2), 58.7 (t, $^3J_{CP} = 9.1$ Hz, CH_2), 59.2 (dd, $^3J_{CP} = 6.0$ Hz, $^1J_{CP} = 9.1$ Hz, CH_2P), 115.8 (s, C^2), 128.9 (d, $^3J_{CP} = 6.8$ Hz, C^m), 129.0 (s, C^p), 130.3 (s, C^3), 132.1 (s, C^4), 133.7 (d, $^2J_{CP} = 18.3$ Hz, C^o), 138.6 (d, $^1J_{CP} = 12.7$ Hz, C^i), 154.7 (s, C^1) ppm.

4.5. Synthesis of *2d*

Hydrazine hydrate (10 ml) was added to a solution of 4-hydroxybenzaldehyde (2.0 g, 13.1 mmol) in THF (10 ml). The solution was stirred for 12 h at room temperature, then allowed to decant. The superior liquid phase was eliminated and the inferior viscous phase was washed with diethylether to obtain compound **2d** as a white powder in 78% yield.

2d. ^1H NMR (DMSO d_6): δ 6.77 (d, $^3J_{HH} = 8.1$ Hz, 2H, C_6H_4), 7.68 (d, $^3J_{HH} = 8.1$ Hz, 2H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (DMSO d_6): δ 115.7 (s, C^2), 124.8 (s, C^4), 129.7 (s, C^3), 160.9 (s, C^1), 166.8 (s, C=O) ppm. Anal. Calcd for $C_7H_8N_2O_2$ (152.15): C, 55.26; H, 5.30; N, 18.41. Found: C, 55.29; H, 5.31; N, 18.40%.

4.6. Synthesis of phosphine *1d*

A mixture of Ph_2PH (29 mmol) and paraformaldehyde (0.89 g, 28 mmol), was heated neat in a closed Schlenck tube at 120 °C for 4 h. After cooling to room temperature, THF was added, and the resulting solution was added via canula to compound **2d** (2.0 g, 13 mmol). The mixture was evaporated to dryness and heated at 85 °C for 12 h, then heated at 60 °C under vacuum to eliminate water. The residue was washed with diethylether to afford **1d** as a white powder in 75% yield.

1d $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −22.9 (s, PPh_2) ppm. ^1H NMR ($CDCl_3$): δ 4.15 (s, 4H, CH_2P), 6.78 (br s, 2H, C_6H_4), 7.25–7.75 (m, 22H, C_6H_4, C_6H_5), 8.39 (br s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 60.4 (dd, $^3J_{CP} = 6.0$ Hz, $^1J_{CP} = 9.0$ Hz, CH_2P), 115.6 (s, C^2), 124.1 (s, C^4), 128.5 (d, $^3J_{CP} = 6.8$ Hz, C^m), 128.8 (s, C^p), 128.9 (s, C^3), 133.0 (d, $^2J_{CP} = 19.0$ Hz, C^o), 137.0 (d, $^1J_{CP} = 11.8$ Hz, C^i), 160.3 (s, C^1), 167.3 (s, C=O) ppm.

4.7. Synthesis of complex *3a*

$[RuCl_2(p\text{-cymene})]_2$ (67 mg, 0.11 mmol) was added to a solution of **1a** (61 mg, 0.22 mmol) in THF (8 ml). The resulting mixture was stirred for 1 h at room temperature, then evaporated to dryness. The residue was washed with

diethyl ether. Complex **3a** was isolated as an orange powder in 89% yield.

3a ^{31}P {^1H} NMR (DMSO d_6): δ 18.7 (s, Ph_2PRu). ^1H NMR (DMSO d_6): δ 0.92 (d, $^3J_{HH} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.73 (s, 3H, CH_3), 2.51 (sept., $^3J_{HH} = 6.9$ Hz, 1H, $CH(CH_3)_2$), 5.18 (d, $^3J_{HH} = 5.9$ Hz, 2H, $CH_{ArCymene}$), 5.27 (d, $^3J_{HH} = 5.9$ Hz, 2H, $CH_{ArCymene}$), 6.76 (d, $^3J_{HH} = 7.3$ Hz, 2H, C_6H_4), 7.35 (m, 6H, C_6H_5), 7.55 (m, 2H, C_6H_4), 7.69 (m, 4H, C_6H_5), 9.96 (s, 1H, OH) ppm. ^{13}C {^1H} NMR (DMSO d_6): δ 19.5 (s, CH_3), 23.7 (s, $CH(CH_3)_2$), 32.1 (s, $CH(CH_3)_2$), 89.0 (d, $J_{CP} = 5.6$ Hz, $CH_{ArCymene}$), 91.7 (d, $J_{CP} = 3.5$ Hz, $CH_{ArCymene}$), 97.4 (s, $CH_3C_{ArCymene}$), 110.7 (s, $(CH_3)_2CHC_{ArCymene}$), 117.2 (d, $^3J_{CP} = 10.8$ Hz, C^2), 124.6 (d, $^1J_{CP} = 50$ Hz, C^4), 130.0 (d, $^3J_{CP} = 9.6$ Hz, C^m), 132.2 (s, C^p), 136.2 (d, $^2J_{CP} = 9.2$ Hz, C^o), 137.2 (d, $^1J_{CP} = 83$ Hz, C^i), 138.3 (d, $^2J_{CP} = 10.9$ Hz, C^3), 161.6 (s, C^1) ppm. Anal. Calcd for $C_{28}H_{29}OPCl_2Ru$ (584.5): C, 57.54; H, 5.00. Found: C, 57.58; H, 4.98%.

4.8. Synthesis of complex *3b*

$[RuCl_2(p\text{-cymene})]_2$ (74 mg, 0.12 mmol) was added to a solution of **1b** (84 mg, 0.24 mmol) in CH_2Cl_2 (10 ml). The resulting mixture was stirred for 1 h at room temperature, then evaporated to dryness. The residue was washed with diethyl ether. Complex **3b** was isolated as an orange powder in 91% yield.

3b ^{31}P {^1H} NMR (DMSO d_6): δ 22.4 (s, Ph_2PRu), ppm. ^1H NMR (DMSO d_6): δ 0.73 (d, $^3J_{HH} = 6.8$ Hz, 6H, $CH(CH_3)_2$), 1.77 (s, 3H, CH_3), 2.06 (s, 3H, CH_3NCH_2), 2.26 (sept., $^3J_{HH} = 6.8$ Hz, 1H, $CH(CH_3)_2$), 4.61 (br s, 2H, CH_2P), 5.23 (d, $^3J_{HH} = 5.8$ Hz, 2H, $CH_{ArCymene}$), 5.45 (d, $^3J_{HH} = 5.8$ Hz, 2H, $CH_{ArCymene}$), 6.57 (d, $^3J_{HH} = 8.0$ Hz, 2H, C_6H_4), 6.65 (s, 1H, CH=N), 6.97 (d, $^3J_{HH} = 8.0$ Hz, 2H, C_6H_4), 7.45 (m, 6H, C_6H_5), 7.88 (m, 4H, C_6H_5), 9.34 (s, 1H, OH) ppm. ^{13}C {^1H} NMR (DMSO d_6): δ 19.4 (s, CH_3), 23.6 (s, $CH(CH_3)_2$), 31.9 (s, $CH(CH_3)_2$), 39.6 (s, CH_3NCH_2), 56.7 (d, $^1J_{CP} = 23.0$ Hz, CH_2P), 88.5 (br s, $CH_{ArCymene}$), 91.6 (d, $^2J_{CP} = 5.0$ Hz, $CH_{ArCymene}$), 96.8 (s, $CH_3C_{ArCymene}$), 110.6 (s, $(CH_3)_2CHC_{ArCy\ mene}$), 117.2 (d, $^3J_{CP} = 10$ Hz, C^2), 128.0 (s, C^3), 130.0 (d, $^3J_{CP} = 9$ Hz, C^m), 132.0 (s, C^p), 132.1 (s, C^4), 136.0 (d, $^1J_{CP} = 9.0$ Hz, C^o), 136.2 (s, CH=N), 136.7 (d, $^1J_{CP} = 83.0$ Hz, C^i), 149.1 (d, $^2J_{CP} = 7.3$ Hz, C_1^1), 161.1 (s, C^1) ppm. Anal. Calcd for $C_{31}H_{35}N_2OPCl_2Ru$ (654.6): C, 56.88; H, 5.39; N, 4.28. Found: C, 56.93; H, 3.43; N, 4.25%.

4.9. Synthesis of complex *4a*

$[RhCl(cod)]_2$ (45 mg, 0.090 mmol) was added to a solution of **1a** (50 mg, 0.180 mmol) in CH_2Cl_2 (10 ml). A yellow precipitate appeared after a few minutes, but the mixture was stirred for 1 h at room temperature. After filtration the precipitate was recovered and washed with CH_2Cl_2. Complex **4a** was isolated as a yellow powder in 93% yield.

4a ^{31}P {^1H} NMR (DMSO d_6): δ 32.5 (d, $^1J_{PRh} = 149.0$ Hz, Ph_2PRh). ^1H NMR (DMSO d_6): δ 1.9 (br s, 4H, CH_2), 2.3 (br s, 4H, CH_2), 3.0 (br s, 2H, CH=CH), 5.3 (br s, 2H, CH=CH), 6.85 (d, $^3J_{HH} = 7.2$ Hz, 2H, C_6H_4), 7.30–7.70 (m, 12H, C_6H_5, C_6H_4). ^{13}C {^1H} NMR (DMSO d_6): δ 28.3 and 32.4 (2 br s, CH_2), 70.1 and 103.8 (2 br s, CH=CH), 115.2 (d, $^3J_{CP} = 10.8$ Hz, C^2), 119.0 (d, $^1J_{CP} = 47.8$ Hz, C^4), 127.9 (d, $^3J_{CP} = 9.8$ Hz, C^m), 130.0 (s, C^p), 131.9 (d, $^1J_{CP} = 42.1$ Hz, C^i), 133.9 (d, $^2J_{CP} = 11.1$ Hz, C^o), 136.7 (d, $^2J_{CP} = 13.1$ Hz, C^3), 159.4 (s, C^1) ppm. Anal. Calcd for $C_{26}H_{27}OPClRh$ (524.8): C, 59.50; H, 5.19. Found: C, 59.51; H, 5.21%.

4.10. Synthesis of dendron *5a-G$_1$*

A solution of compound **1a** (390 mg, 1.40 mmol) in THF (20 ml) was added to sodium hydride (33 mg, 1.40 mmol). The resulting suspension was stirred at room temperature until it became a solution then 240 mg (0.28 mmol) of $\mathbf{G}_1$ were added. The resulting mixture was stirred overnight at room temperature, then centrifuged and evaporated to dryness. The resulting powder was washed thrice with THF/pentane (1/5) to afford **5a-G$_1$** as a white powder in 92% yield.

5a-G$_1$: ^{31}P {^1H} NMR ($CDCl_3$): δ −3.1 (s, P'_1), 14.9 (d, $^2J_{PP} = 30.0$ Hz, P'_0), 56.2 (d, $^2J_{PP} = 30.0$ Hz, P_0), 65.2 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ 3.37 (d, $^3J_{HP} = 11.0$ Hz, 6H, N–CH_3), 6.12 (ddd, $^3J_{HP} = 24.1$ Hz, $^3J_{HHa} = 18.3$ Hz, $^2J_{HH} = 1.1$ Hz, 1H, H_c), 6.41 (ddd, $^3J_{HP} = 46.0$ Hz, $^3J_{HHa} = 12.5$ Hz, $^2J_{HH} = 1.1$ Hz, 1H, H_b), 6.8 (dddd, $^2J_{HP} = 25.3$ Hz, $^3J_{HHc} = 18.3$ Hz, $^3J_{HHb} = 12.5$ Hz, $^4J_{HP} = 1.1$ Hz, 1H, H_a), 7.2–7.9 (m, 76H, H_{Ar}, CH=N) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ 32.8 (d, $^2J_{CP} = 13.0$ Hz, N–CH_3), 121.4 (d, $^3J_{CP} = 5$ Hz, C_1^2), 121.9 (d, $^3J_{CP} = 5$ Hz, C_0^2), 127.7 (dd, $^1J_{CP} = 91.0$ Hz, $^3J_{CP} = 4.5$ Hz, C_0^i), 127.9 (s, C_0^3), 128.4 (d, $^3J_{CP} = 7.0$ Hz, C_1^m), 128.6 (d, $^3J_{CP} = 13.0$ Hz, C_0^m), 128.8 (s, C_1^p), 130.3 (s, C_0^4), 132.0 (d, $^2J_{CP} = 11.0$ Hz, C_0^o), 132.6 (d, $^4J_{CP} = 2.3$ Hz, C_0^p), 133.0 (d, $^1J_{CP} = 10.1$ Hz, C_1^4), 133.5 (d, $^2J_{CP} = 19.5$ Hz, C_1^o), 135.0 (d, $^2J_{CP} = 20.5$ Hz, C_1^3), 136.6 (d, $^1J_{CP} = 10.5$ Hz, C_1^i), 136.7 (s, CH_2=), 140.1 (d, $^3J_{CP} = 13.7$ Hz, CH=NNP$_1$), 150.8 (d, $^2J_{CP} = 8.0$ Hz, C_1^1), 153.1 (d, $^2J_{CP} = 10.5$ Hz, C_0^1) ppm. Anal. Calcd for $C_{102}H_{85}N_5O_6P_8S_3$ (1821): C, 67.29; H, 4.71; N, 3.85. Found: C, 67.12; H, 4.63; N, 3.80%.

4.11. Synthesis of dendron *5a-G$_2$*

A solution of compound **1a** (420 mg, 1.51 mmol) in THF (20 ml) was added to sodium hydride (37 mg, 1.51 mmol). The resulting suspension was stirred for 30 min at room temperature to afford a solution, which was added to 300 mg (0.167 mmol) of $\mathbf{G}_2$. The resulting mixture was stirred overnight at room temperature, then centrifuged and evaporated to dryness. The resulting powder was washed 3 times with THF/pentane (1/5) to afford **5a-G$_2$** as a white powder in 90% yield.

5a-G$_2$: ^{31}P {^{1}H} NMR ($CDCl_3$): δ −2.9 (s, P′$_2$), 14.0 (d, $^2J_{PP}$ = 31.9 Hz, P′$_0$), 56.5 (d, $^2J_{PP}$ = 31.9 Hz, P$_0$), 65.2 (s, P$_2$), 65.9 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$): δ 3.34 (d, $^3J_{HP}$ = 10.5 Hz, 12H, P$_2$–N–CH_3), 3.37 (d, $^3J_{HP}$ = 10.3 Hz, 6H, P$_1$–N–CH_3), 6.12 (m, 1H, H$_c$), 6.42 (m, 1H, H$_b$), 6.8 (m, 1H, H$_a$), 7.1–7.8 (m, 152H, H$_{Ar}$, CH=N) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 32.8 (d, $^2J_{CP}$ = 13.0 Hz, P$_1$–N–CH_3, P$_2$–N–CH_3), 121.2 (br s, C_2^2), 121.8 (br s, C_0^2, C_1^2), 127.9 (s, C_0^3), 128.1 (s, C_1^3), 128.4 (d, $^3J_{CP}$ = 7.0 Hz, C_0^m, C_2^m), 128.8 (s, C_2^p), 130.1 (s, C_0^4), 130.7 (s, C_1^4), 132.0 (d, $^2J_{CP}$ = 10.1 Hz, C_0^o), 132.5 (s, C_0^p), 133.5 (d, $^2J_{CP}$ = 19.8 Hz, C_2^o), 133.8 (d, $^1J_{CP}$ = 10.0 Hz, C_2^4), 134.8 (d, $^2J_{CP}$ = 20.4 Hz, C_2^3), 136.7 (d, $^1J_{CP}$ = 10.6 Hz, C_2^i), 138.7 (d, $^3J_{CP}$ = 13.7 Hz, CH=NNP$_2$), 139.2 (d, $^3J_{CP}$ = 13.7 Hz, CH=NNP$_1$), 150.9 (d, $^2J_{CP}$ = 7.5 Hz, C_2^1), 151.1 (d, $^2J_{CP}$ = 8.0 Hz, C_1^1), 152.9 (d, $^2J_{CP}$ = 10.2 Hz, C_0^1) ppm. Anal. Calcd for $C_{206}H_{173}N_{13}O_{14}P_{16}S_7$ (3775): C, 65.55; H, 4.62; N, 4.82. Found: C, 65.39; H, 4.58; N, 4.77%.

4.12. Synthesis of dendron 5b-G$_1$

A solution of the sodium salt of **1b** (388 mg, 1.11 mmol) (obtained by reaction of NaH with **1b**) in THF (20 ml) was added to a solution of **G**$_1$ (216 mg, 0.25 mmol) in THF (10 ml). The resulting mixture was stirred for 12 h at room temperature then centrifuged and evaporated to dryness. The residue was dissolved in THF and precipitated with pentane (repeated 3 times). Compound **5b-G**$_1$ was isolated as a white powder in 95% yield.

5b-G$_1$: ^{31}P {^{1}H} NMR ($CDCl_3$): δ −19.7 (s, P′$_1$), 14.8 (d, $^2J_{PP}$ = 30.4 Hz, P′$_0$), 56.1 (d, $^2J_{PP}$ = 30.4 Hz, P$_0$), 66.3 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$): δ 2.94 (s, 12H, CH_3NCH$_2$), 3.31 (d, $^3J_{HP}$ = 10.7 Hz, 6H, P$_1$–N–CH_3), 4.17 (d, $^2J_{HP}$ = 3.1 Hz, 8H, CH_2), 6.10 (ddd, $^3J_{HP}$ = 24.1 Hz, $^3J_{HHa}$ = 18.3 Hz, $^2J_{HH}$ = 1.2 Hz, 1H, H$_c$), 6.34 (ddd, $^3J_{HP}$ = 45.9 Hz, $^3J_{HHa}$ = 12.4 Hz, $^2J_{HH}$ = 1.2 Hz, 1H, H$_b$), 6.80 (dddd, $^2J_{HP}$ = 25.2 Hz, $^3J_{HHc}$ = 18.3 Hz, $^3J_{HHb}$ = 12.4 Hz, $^4J_{HP}$ = 1.2 Hz, 1H, H$_a$), 7.0–7.9 (m, 80H, H$_{Ar}$, CH=N) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 33.1 (d, $^2J_{CP}$ = 13.0 Hz, P$_1$–N–CH_3), 38.9 (d, $^3J_{CP}$ = 6.7 Hz, CH_3NCH$_2$), 61.1 (d, $^1J_{CP}$ = 10.6 Hz, CH_2), 121.5 (d, $^3J_{CP}$ = 4.7 Hz, C_1^2), 122.0 (d, $^3J_{CP}$ = 4.9 Hz, C_0^2), 126.6 (s, C_1^3), 127.6 (dd, $^1J_{CP}$ = 91.0 Hz, $^3J_{CP}$ = 4.0 Hz, C_0^i), 128.0 (s, C_0^3), 128.5 (d, $^3J_{CP}$ = 6.7 Hz, C_1^m), 128.7 (s, C_1^p), 128.8 (d, $^3J_{CP}$ = 13.0 Hz, C_0^m), 131.0 (s, C_1^4), 131.1 (s, C_0^4), 132.2 (d, $^2J_{CP}$ = 10.9 Hz, C_0^o), 132.7 (d, $^4J_{CP}$ = 2.0 Hz, C_0^p), 133.1 (d, $^1J_{CP}$ = 18.6 Hz, C_1^o), 134.2 (s, C_1^4-CH=N), 136.8 (s, CH_2=), 137.6 (d, $^1J_{CP}$ = 13.3 Hz, C_1^i), 139.0 (d, $^3J_{CP}$ = 13.7 Hz, CH=NNP$_1$), 149.7 (d, $^2J_{CP}$ = 7.3 Hz, C_1^1), 153.1 (d, $^2J_{CP}$ = 9.5 Hz, C_0^1) ppm.

4.13. Synthesis of dendron 5c-G$_1$

A solution of **G**$_1$ (179 mg, 0.2 mmol) in THF (5 ml) was added to a solution in THF (5 ml) of the sodium salt of **1c** (466 mg, 0.83 mmol) (obtained by reaction of NaH with **1c**). The resulting mixture was stirred for 1 day at room temperature, then evaporated to dryness. The residue was dissolved in THF, filtered through celite, and evaporated again. Washings with diethyl ether and pentane afforded **5c-G**$_1$ as a white powder in 91% yield.

5c-G$_1$: ^{31}P {^{1}H} NMR ($CDCl_3$): δ −25.1 (s, P′$_1$), 14.9 (d, $^2J_{PP}$ = 28.5 Hz, P′$_0$), 56.3 (d, $^2J_{PP}$ = 28.5 Hz, P$_0$), 66.8 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$): δ 2.61 (t, $^3J_{HH}$ = 8.0 Hz, 8H, NCH_2CH_2), 3.09 (t, $^3J_{HH}$ = 8.0 Hz, 2H, NCH_2CH_2), 3.28 (d, $^3J_{HP}$ = 10.4 Hz, 6H, P$_1$–N–CH_3), 3.62 (br s, 16H, CH_2P), 6.10 (dd, $^3J_{HP}$ = 24 Hz, $^3J_{HHa}$ = 17 Hz, 1H, H$_c$), 6.33 (dd, $^3J_{HP}$ = 47 Hz, $^3J_{HHa}$ = 12 Hz, 1H, H$_b$), 6.68 (d, $^3J_{HH}$ = 8.2 Hz, 4H, H–C_0^2), 6.87 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H–C_0^3)), 6.91 (d, $^3J_{HH}$ = 8.0 Hz, 8H, H–C_1^2), 7.04 (d, $^3J_{HH}$ = 8.0 Hz, 8H, H–C_1^3), 7.2-7.8 (m, 116H, H$_{Ar}$, CH=N) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 32.0 (s, NCH_2CH_2), 33.1 (d, $^2J_{CP}$ = 13.0 Hz, P$_1$–N–CH_3), 57.7 (t, $^3J_{CP}$ = 8.9 Hz, CH_2), 58.6 (dd, $^3J_{CP}$ = 5.9 Hz, $^1J_{CP}$ = 7.9 Hz, CH_2P), 115.3 (s, C_1^2), 121.2 (d, $^3J_{CP}$ = 3.0 Hz, C_1^2), 122.0 (br s, C_0^2),128.4 (d, $^3J_{CP}$ = 7.0 Hz, C^m), 128.5 (s, C^p), 128.0 (s, C_0^3), 128.9 (d, $^3J_{CP}$ = 10.0 Hz, C_0^m), 129.8 (s, C_1^3), 131.2 (s, C_0^4), 132.2 (d, $^2J_{CP}$ = 11.0 Hz, C_0^o), 133.1 (d, $^2J_{CP}$ = 18.4 Hz, C_1^o), 136.8 (s, CH_2=), 137.2 (s, C_1^4), 138.1 (d, $^1J_{CP}$ = 12.7 Hz, C_1^i), 138.2 (d, $^1J_{CP}$ = 12.7 Hz, C_0^i), 138.9 (d, $^3J_{CP}$ = 12.6 Hz, CH=NNP$_1$), 148.7 (d, $^2J_{CP}$ = 6.8 Hz, C_1^1), 153.0 (d, $^2J_{CP}$ = 8.6 Hz, C_0^1) ppm.

4.14. Synthesis of complex 6a-G$_1$

[RuCl$_2$(*p*-cymene)]$_2$ (125 mg, 0.20 mmol) was added to a solution of **5a-G**$_1$ (187 mg, 0.10 mmol) in THF (10 ml). The resulting mixture was stirred for 2 h at room temperature, then evaporated to dryness. The residue was washed with pentane. Complex **6a-G**$_1$ was isolated as an orange powder in 83% yield.

6a-G$_1$: ^{31}P {^{1}H} NMR ($CDCl_3$): δ 14.7 (d, $^2J_{PP}$ = 29.4 Hz, P′$_0$), 27.2 (s, Ph_2PRu), 55.6 (d, $^2J_{PP}$ = 29.4 Hz, P$_0$), 64.2 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$): δ 1.06 (d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 1.81 (s, 12H, CH_3), 2.79 (sept., $^3J_{HH}$ = 7.0 Hz, 4H, CH(CH$_3$)$_2$), 3.33 (d, $^3J_{HP}$ = 10.8 Hz, 6H, P$_1$–N–CH_3), 4.95 (d, $^3J_{HH}$ = 6.0 Hz, 8H, $CH_{ArCymene}$), 5.16 (d, $^3J_{HH}$ = 6.0 Hz, 8H, $CH_{ArCymene}$), 6.3 (m, 1H, H$_c$), 6.8 (m, 2H, H_2C=), 7.1–7.8 (m, 76H, H$_{Ar}$, CH=N) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 17.8 (s, CH_3), 21.9 (s, CH(CH_3)$_2$), 30.3 (s, CH(CH$_3$)$_2$), 32.8 (d, $^2J_{CP}$ = 13.0 Hz, P$_1$–N–CH_3), 87.2 (d, J_{CP} = 5.2 Hz, $CH_{ArCymene}$), 89.1 (s, $CH_{ArCymene}$), 96.0 (s, $CH_3C_{ArCymene}$), 111.2 (s, $(CH_3)_2CHC_{ArCymene}$), 120.7 (m, C_1^2), 122.0 (br s, C_0^2), 128.1 (d, $^3J_{CP}$ = 9.6 Hz, C_1^m), 128.7 (s, C_0^3), 128.8 (d, $^3J_{CP}$ = 12.4 Hz, C_0^m), 130.3 (br d, $^1J_{CP}$ = 46.0 Hz, C_1^4), 130.4 (s, C_1^p), 132.1 (d, $^2J_{CP}$ = 10.1 Hz, C_0^o), 132.8 (br s, C_0^p), 133.5 (d, $^1J_{CP}$ = 50.0 Hz, C_1^i), 134.2 (d, $^2J_{CP}$ = 9.4 Hz, C_1^o), 135.9 (d, $^2J_{CP}$ = 10.1 Hz, C_1^3), 136.9 (s, CH_2=), 139.8 (d, $^3J_{CP}$ = 13.0 Hz, CH=NNP$_1$), 152.0 (br s, C_1^1), 153.1 (br s, C_0^1) ppm. Anal. Calcd for $C_{142}H_{141}N_5O_6P_8S_3Cl_8Ru_4$ (3046): C, 56.00; H, 4.67; N, 2.30. Found: C, 56.07; H, 4.71; N, 2.28%.

4.15. Synthesis of complex **6b-G$_1$**

[$RuCl_2$(*p*-cymene)]$_2$ (62 mg, 0.10 mmol) was added to a solution of **5b-G$_1$** (105 mg, 0.05 mmol) in THF (10 ml). The resulting mixture was stirred for 4 h at room temperature, then evaporated to dryness. The residue was washed with pentane. Complex **6b-G$_1$** was isolated as an orange powder in 94% yield.

6b-G$_1$: ^{31}P {^{1}H} NMR ($CDCl_3$): δ 15.0 (d, $^2J_{PP} = 30.0$ Hz, P′$_0$), 29.2 (s, Ph_2PRu), 56.1 (d, $^2J_{PP} = 30.0$ Hz, P$_0$), 62.3 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$): δ 0.84 (d, $^3J_{HH} = 7.0$ Hz, 12H, CH(C*H*$_3$)$_2$), 0.87 (d, $^3J_{HH} = 7.0$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.85 (s, 12H, CH_3), 2.15 (s, 12H, C*H*$_3$NCH$_2$), 2.47 (sept., $^3J_{HH} = 7.0$ Hz, 4H, C*H*(CH$_3$)$_2$), 3.31 (d, $^3J_{HP} = 10.4$ Hz, 6H, P$_1$–N–CH$_3$), 4.83 (br s, 8H, CH_2P), 5.10 (m, 8H, $CH_{ArCymene}$), 5.25 (m, 8H, $CH_{ArCymene}$), 6.00–6.75 (m, 3H, CH_2=CH), 6.95–8.10 (m, 76H, H_{Ar}, CH=N) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 17.4 (s, CH_3), 21.4 (s, CH(*C*H$_3$)$_2$), 29.9 (s, *C*H(CH$_3$)$_2$), 33.1 (d, $^2J_{CP} = 12.7$ Hz, P$_1$–N–CH$_3$), 38.6 (s, *C*H$_3$NCH$_2$), 54.9 (d, $^1J_{CP} = 22.9$ Hz, CH_2P), 85.6 (s, $CH_{ArCymene}$), 89.9 (d, $^2J_{CP} = 5.5$ Hz, $CH_{ArCymene}$), 94.1 (s, $CH_3C_{ArCymene}$), 108.0 (s, $(CH_3)_2CHC_{ArCymene}$), 121.2 (d, $^3J_{CP} = 4.0$ Hz, C$_1^2$), 122.0 (d, $^3J_{CP} = 4.0$ Hz, C$_0^2$), 126.0 (s, C$_1^3$), 127.5 (s, C$_0^3$), 128.0 (d, $^3J_{CP} = 8.5$ Hz, C$_1^m$), 128.8 (d, $^3J_{CP} = 12.8$ Hz, C$_0^m$), 130.4 (d, $^1J_{CP} = 97.1$ Hz, C$_1^i$), 130.7 (s, C$_1^p$), 131.1 (s, C$_1^4$), 131.3 (s, C$_0^4$), 132.1 (d, $^2J_{CP} = 10.8$ Hz, C$_0^o$), 132.7 (s, C$_0^p$), 134.2 (s, C$_1^4$*C*H=N), 134.4 (d, $^1J_{CP} = 7.5$ Hz, C$_1^o$), 136.9 (s, CH_2=), 139.0 (d, $^3J_{CP} = 12.6$ Hz, CH=NNP$_1$), 149.1 (d, $^2J_{CP} = 7.3$ Hz, C$_1^1$), 153.1 (d, $^2J_{CP} = 9.5$ Hz, C$_0^1$) ppm. Anal. Calcd for $C_{154}H_{165}N_{13}O_6P_8S_3Cl_8Ru_4$ (3326): C, 55.61; H, 5.00; N, 5.48. Found: C, 55.68; H, 5.03; N, 5.45%.

4.16. Synthesis of dendron **7a-G$_1$**

Ethylenediamine (0.44 ml, 6.6 mmol) was rapidly added to a solution of dendron **5a-G$_1$** (120 mg, 0.066 mmol) in THF (15 ml) under vigorous stirring. After 3h at room temperature, the solution was evaporated to dryness. The residue was washed 3 times with a mixture THF/pentane (1:5) to afford the dendron **7a-G$_1$** as a white powder in 92% yield.

7a-G$_1$: ^{31}P {^{1}H} NMR ($CDCl_3$): δ −2.9 (s, P′$_1$), 21.4 (d, $^2J_{PP} = 34.0$ Hz, P′$_0$), 56.0 (d, $^2J_{PP} = 34.0$ Hz, P$_0$), 65.5 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$): δ 2.40–2.65 (m, 4H, NCH_2CH_2N), 2.70–2.95 (m, 4H, CH_2CH_2P), 3.35 (d, $^3J_{HP} = 10.6$ Hz, 6H, P$_1$–N–CH$_3$), 7.10–7.70 (m, 76H, H_{Ar}, CH=N) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 27.3 (d, $^1J_{CP} = 64.7$ Hz, $CH_2P'_0$), 32.8 (d, $^2J_{CP} = 13.5$ Hz, P$_1$–N–CH$_3$), 41.1 and 42.1 (2s, $H_2NCH_2CH_2NHCH_2$), 51.6 (s, $H_2NCH_2CH_2NH$), 121.3 (m, C$_1^2$), 121.8 (d, $^3J_{CP} = 4.5$ Hz, C$_0^2$), 127.8 (s, C$_0^3$), 128.3 (s, C$_1^p$), 128.5 (d, $^3J_{CP} = 10.2$ Hz, C$_1^m$), 128.7 (d, $^3J_{CP} = 12.9$ Hz, C$_0^m$), 130.7 (s, C$_0^4$), 131.1 (d, $^2J_{CP} = 10.3$ Hz, C$_0^o$), 131.9 (dd, $^1J_{CP} = 101.0$ Hz, $^3J_{CP} = 6.0$ Hz, C$_0^i$), 132.4 (d, $^4J_{CP} = 3.0$ Hz, C$_0^p$), 133.5 (d, $^2J_{CP} = 19.3$ Hz, C$_1^o$), 133.8 (d, $^1J_{CP} = 11.0$ Hz, C$_1^4$), 134.8 (d, $^2J_{CP} = 20.5$ Hz, C$_1^3$), 136.7 (d, $^1J_{CP} = 10.6$ Hz, C$_1^i$), 136.8 (s, CH_2=), 139.2 (d, $^3J_{CP} = 13.9$ Hz, CH=NNP$_1$), 151.0 (d, $^2J_{CP} = 7.3$ Hz, C$_1^1$), 152.8 (d, $^2J_{CP} = 9.3$ Hz, C$_0^1$) ppm. Anal. Calcd for $C_{104}H_{91}N_7O_6P_8S_3$ (1879): C, 66.48; H, 4.88; N, 5.22. Found: C, 66.34; H, 4.81; N, 5.17%.

4.17. Synthesis of dendron **7b-G$_1$**

Ethylenediamine (0.50 ml, 7.5 mmol) was rapidly added to a solution of dendron **5b-G$_1$** (174 mg, 0.08 mmol) in THF (15 ml) under vigorous stirring. After 2h30 at room temperature, the solution was evaporated to dryness. The residue was washed 3 times with a mixture THF/pentane (1:5) to afford the dendron **7b-G$_1$** as a white powder in 84% yield.

7b-G$_1$: ^{31}P {^{1}H} NMR ($CDCl_3$): δ −19.6 (s, P′$_1$), 21.1 (d, $^2J_{PP} = 33.8$ Hz, P′$_0$), 55.7 (d, $^2J_{PP} = 33.8$ Hz, P$_0$), 66.4 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$): δ 2.40–2.65 (m, 4H, NCH_2CH_2N), 2.80–3.05 (m, 4H, CH_2CH_2P), 2.93 (s, 12H, C*H*$_3$NCH$_2$), 3.30 (d, $^3J_{HP} = 10.6$ Hz, 6H, P$_1$–N–CH$_3$), 4.17 (d, $^2J_{HP} = 3.1$ Hz, 8H, CH_2P), 7.00-7.70 (m, 80H, H_{Ar}, CH=N) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 27.8 (d, $^1J_{CP} = 64.9$ Hz, $CH_2P'_0$), 33.4 (d, $^2J_{CP} = 12.8$ Hz, P$_1$–N–CH$_3$), 39.3 (d, $^3J_{CP} = 6.8$ Hz, *C*H$_3$NCH$_2$), 41.7 and 42.7 (2s, $H_2NCH_2CH_2NHCH_2$), 52.1 (s, H_2NCH_{20}-*C*H$_2$NH), 61.4 (d, $^1J_{CP} = 7.5$ Hz, NCH_2P), 121.8 (br s, C$_1^2$), 122.4 (br s, C$_0^2$), 127.0 (s, C$_1^3$), 128.4 (s, C$_0^3$), 128.9 (d, $^3J_{CP} = 7.0$ Hz, C$_1^m$), 129.1 (s, C$_1^p$), 129.3 (d, $^3J_{CP} = 15.0$ Hz, C$_0^m$), 131.3 (s, C$_0^4$, C$_1^4$), 131.7 (d, $^2J_{CP} = 8.0$ Hz, C$_0^o$), 133.0 (s, C$_0^p$), 133.5 (d, $^1J_{CP} = 15.1$ Hz, C$_1^o$), 134.6 (s, C$_1^4$–*C*H=N), 138.1 (d, $^1J_{CP} = 15.1$ Hz, C$_1^i$), 139.4 (d, $^3J_{CP} = 15.1$ Hz, CH=NNP$_1$), 150.0 (d, $^2J_{CP} = 7.5$ Hz, C$_1^1$), 152.7 (br s, C$_0^1$) ppm.

4.18. Synthesis of dendron **8a-G$_2$**

Aminopentanol (308 mg, 20 equivalents) was rapidly added to a solution of dendron **5a-G$_2$** (560 mg, 0.148 mmol) in THF (15 ml). The resulting solution was heated in a sealed Schlenck at 70 °C overnight then evaporated to dryness. The residue was washed 4 times with a mixture THF/pentane (1:5) then ether/pentane (1:2) to afford the dendron **8a-G$_2$** as a white powder in 90% yield.

8a-G$_2$. ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −3.1 (s, P′$_2$), 21.3 (d, $^2J_{PP} = 32.6$ Hz, P′$_0$), 55.8 (d, $^2J_{PP} = 32.6$ Hz, P$_0$), 65.0 (s, P$_2$), 66.1 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.30–1.70 (m, 6H, HO–CH_2–*CH*$_2$–*CH*$_2$–*CH*$_2$–CH_2–NH), 2.47 (t, $^3J_{HH} = 6.3$ Hz, 2H, –CH_2–CH_2–*CH*$_2$–NH), 2.7–3.0 (m, 4H, CH_2–CH_2–P′$_0$), 3.34 (d, $^3J_{HP} = 10.5$ Hz, 18H, N–CH$_3$), 3.52 (t, $^3J_{HH} = 6.4$ Hz, 2H, HO–*CH*$_2$–), 7.1–7.8 (m, 152H, H_{Ar}, CH=N) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 23.1 (s, C_cH_2), 27.2 (d, $^1J_{CP} = 58$ Hz, CH_2–P′$_0$), 29.3 (s, C_dH_2), 32.2 (d, $^2J_{CP} = 12.8$ Hz, N–CH$_3$), 34.0 (s, C_bH_2), 42.3 (s, *CH*$_2$–CH_2–P′$_0$), 49.1 (s, C_eH_2), 62.3 (s, C_aH_2), 121.3 (“t”, $^3J_{CP'3} = {}^3J_{CP2} = 5.8$ Hz, C$_2^2$), 121.8 (d, $^3J_{CP} = 5.1$ Hz, C$_0^2$, C$_1^2$), 127.9 (s, C$_0^3$), 128.1 (s, C$_1^3$), 128.4

(d, $^3J_{CP} = 7.1$ Hz, C_0^m, C_2^m), 128.7 (s, C_2^p), 128.8 (dd, $^3J^{CP} = 7.1$ Hz, $^1J_{CP} = 95.1$ Hz, C_0^i), 130.7 (s, C_0^4), 131.2 (d, $^2J_{CP} = 10.1$ Hz, C_0^o), 131.9 (s, C_1^4), 132.4 (s, C_0^p), 133.5 (d, $^2J_{CP} = 19.5$ Hz, C_2^o), 133.9 (s, $^1J_{CP} = 9.8$ Hz, C_2^4), 134.9 (d, $^2J_{CP} = 20.4$ Hz, C_2^3), 136.7 (d, $^1J_{CP} = 10.4$ Hz, C_2^i), 138.7 (d, $^3J_{CP} = 13.6$ Hz, CH=NNP$_2$), 139.4 (d, $^3J_{CP} = 14.7$ Hz, CH=NNP$_1$), 151.0 (d,^{2} $J_{CP} = 7.6$ Hz, C_2^1), 151.1 (d,^{2} $J_{CP} = 7.7$ Hz, C_1^1), 152.9 (d,^{2} $J_{CP} = 8.8$ Hz, C_0^1). Anal. Calcd for $C_{211}H_{186}N_{14}O_{15}P_{16}S_7$ (3878): C, 65.35; H, 4.83; N, 5.06. Found: C, 65.28; H, 4.79; N, 4.98%.

4.19. Synthesis of complex **9b-G$_1$**

A solution of [RuCl$_2$(*p*-cymene)]$_2$ (76 mg, 0.124 mmol) in CH_2Cl_2 (5 ml) was added to a solution of **7b-G$_1$** (134 mg, 0.062 mmol) in CH_2Cl_2 (15 ml). After stirring for 1h at room temperature, the solution was evaporated to dryness. The residue was washed several times with diethylether, to afford **9b-G$_1$** as an orange powder in 80% yield.

9b-G$_1$: ^{31}P {^{1}H} NMR ($CDCl_3$): δ 20.8 (d, $^2J_{PP} = 33.7$ Hz, P′$_0$), 29.1 (s, Ph_2PRu), 55.0 (d, $^2J_{PP} = 33.7$ Hz, P$_0$), 66.3 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$): δ 0.84 (d, $^3J_{HH} = 6.3$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.84 (s, 12H, CH$_3$), 2.14 (s, 12H, C*H*$_3$NCH$_2$), 2.46 (m, 4H, C*H*(CH$_3$)$_2$), 2.40–2.65 (m, 4H, CH$_2$N), 2.80–3.05 (m, 4H, CH$_2$N), 2.92 (s, 12H, C*H*$_3$NCH$_2$), 3.30 (d, $^3J_{HP} = 10.4$ Hz, 6H, P$_1$–N–CH$_3$), 4.82 (br s, 8H, NCH$_2$P), 5.10 (m, 8H, CH$_{ArCymene}$), 5.27 (d, $^2J_{HP} = 6.0$ Hz 8H, CH$_{ArCymene}$), 6.53 (s, 4H, C$_1^4$CH=N), 6.90–8.00 (m, 80H, H$_{Ar}$, CH=N) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 17.4 (s, CH$_3$), 21.4 (s, CH(*C*H$_3$)$_2$), 27.0 (d, $^1J_{CP} = 65$ Hz, CH$_2$P′$_0$), 29.9 (s, *C*H(CH$_3$)$_2$), 33.1 (d, $^2J_{CP} = 12.4$ Hz, P$_1$–N–CH$_3$), 38.6 (s, *C*H$_3$NCH$_2$), 54.9 (d, $^1J_{CP} = 23.1$ Hz, NCH$_2$P), 85.5 (s, CH$_{ArCymene}$), 89.9 (br s, CH$_{ArCymene}$), 94.1 (s, CH$_3$*C*$_{ArCymene}$), 109.0 (s, (CH$_3$)$_2$CH*C*$_{ArCymene}$), 121.2 (br s, C_1^2), 122.0 (br s, C_0^2), 126.0 (s, C_1^3), 126.6 (s, C_0^3), 128.0 (d, $^3J_{CP} = 8.4$ Hz, C_1^m), 128.9 (d, $^3J_{CP} = 12.0$ Hz, C_0^m), 130.1 (d, $^1J_{CP} = 98.0$ Hz, C_1^i), 130.7 (s, C_1^p), 131.3 (s, C_1^4), 131.6 (s, C_0^4), 132.4 (d, $^2J_{CP} = 10.0$ Hz, C_0^o), 132.4 (s, C_0^p), 134.3 (m, C_1^o, C_1^4*C*H=N), 139.0 (br s, CH=NNP$_1$), 149.1 (br s, C_1^1), 152.9 (d, $^2J_{CP} = 9.5$ Hz, C_0^1) ppm. Anal. Calcd for $C_{156}H_{173}N_{15}O_6P_8S_3Cl_8Ru_4$ (3386): C, 55.34; H, 5.15; N, 6.21. Found: C, 55.48; H, 5.21; N, 6.16%.

4.20. Synthesis of complex **10a-G$_2$**

A solution of [RhCl(cod)]$_2$ (246 mg, 0.500 mmol) in CH_2Cl_2 (5 ml) was added to a solution of **8a-G$_2$** (484 mg, 0.125 mmol) in CH_2Cl_2 (15 ml). After stirring for 2h at room temperature, the solution was evaporated to dryness. The residue was washed several times with CH_2Cl_2/pentane, to afford **10a-G$_2$** as a yellow powder in 80% yield.

10a–G$_2$: ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 20.5 (d, $^2J_{PP} = 32.9$ Hz, P′$_0$), 33.5 (d, $^1J_{PRh} = 151.0$ Hz, P′$_2$ Rh), 55.3 (d,$^2J_{PP} = 32.9$ Hz, P$_0$), 64.1 (s, P$_2$), 66.1 (s, P$_1$) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.30–1.70 (m, 6H, HO–CH$_2$–*CH*$_2$– *CH*$_2$–CH$_2$-NH), 1.96 (m, 32H, CH$_2$cod), 2.36 (br s, 34H, CH$_2$cod, –CH$_2$–CH$_2$–*CH*$_2$–NH), 2.7–3.0 (m, 4H, CH$_2$–CH$_2$–P′$_0$), 3.09 (br s, 16H, CHcod), 3.34 (d, $^3J_{HP} = 10.5$ Hz, 18H, N–CH$_3$), 3.52 (br s, 2H, HO–*CH*$_2$), 5.53 (br s, 16H, CHcod), 7.1–7.9 (m, 152H, H$_{Ar}$, CH=N) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 23.3 (s, C$_c$H$_2$), 27.3 (d, $^1J_{CP} = 56.0$ Hz, CH$_2$-P′$_0$), 29.1 (s, CH$_2$cod), 29.4 (s, C$_d$H$_2$), 32.3 (d, $^2J_{CP} = 13.0$ Hz, N–CH$_3$), 33.4 (s, CH$_2$cod), 34.1 (s, C$_b$H$_2$), 42.4 (s, *CH*$_2$–CH$_2$–P′$_0$), 49.3 (s, C$_e$H$_2$), 62.4 (s, C$_a$H$_2$), 71.2 (br s, CHcod), 105.0 (br s, CHcod), 121.3 (m, C_2^2), 121.8 (br s, C_0^2, C_1^2), 128.1 (s, C_0^3, C_1^3), 128.5 (d, $^3J_{CP} = 7.0$ Hz, C_2^m), 128.7 (br s, C_0^m) 130.7 (s, C_2^p, C_0^4), 131.2 (d, $^2J_{CP} = 10.1$ Hz, C_0^o), 131.7 (d, $^1J_{CP} = 42.1$ Hz, C_2^i), 131.9 (s, C_1^4), 132.4 (s, C_0^p), 134.5 (d, $^2J_{CP} = 11.5$ Hz, C_2^o), 137.1 (d, $^2J_{CP} = 13.4$ Hz, C_2^3), 139.9 (m, CH=NNP), 151.7 (br s, C_1^1), 152.6 (d, $^2J_{CP} = 7.0$ Hz, C_2^1), 153.1 (br s, C_0^1). Anal. Calcd for $C_{275}H_{282}Cl_8N_{14}O_{15}P_{16}Rh_8S_7$ (5850.2): C, 56.46; H, 4.86; N, 3.35. Found: C, 56.53; H, 4.89; N, 3.28.

Acknowledgements

Thanks are due to the European Community through the contract MRTN-CT-2003-503864 (AQUACHEM) for a grant to P. Servin, and through the Marie Curie training site HPMTGH010039808 for a grant to I. Angurell. This work was also supported by the CNRS.

References

[1] C.J. Hawker, J.M.J. Fréchet, J. Am. Chem. Soc. 112 (1990) 7638.
[2] J.S. Moore, Z. Xu, Macromolecules 24 (1991) 5893.
[3] G.R. Newkome, F. Vögtle, C.N. Moorefield, Dendrimers and Dendrons, John Wiley and Sons, Weinheim Germany, 2001.
[4] J.M.J. Fréchet, D.A. Tomalia, Dendrimers and Other Dendritic Polymers, John Wiley and Sons, Chichester, UK, 2001.
[5] A.M. Caminade, A. Maraval, J.P. Majoral, Eur. J. Inorg. Chem. (2006) 887.
[6] Y. Ishida, M. Jikei, M.A. Kakimoto, Macromolecules 33 (2000) 3202.
[7] K. Sivanandan, B.S. Sandanaraj, S. Thayumanavan, J. Org. Chem. 69 (2004) 2937.
[8] V. Maraval, R. Laurent, B. Donnadieu, M. Mauzac, A.M. Caminade, J.P. Majoral, J. Am. Chem. Soc. 122 (2000) 2499.
[9] V. Maraval, R. Laurent, S. Merino, A.M. Caminade, J.P. Majoral, Eur. J. Org. Chem. (2000) 3555.
[10] A.M. Caminade, V. Maraval, R. Laurent, J.P. Majoral, Curr. Org. Chem. 6 (2002) 739.
[11] P.A. Chase, R.J.M. Klein Gebbink, G. van Koten, J. Organomet. Chem. 689 (2004) 4016.
[12] B. Helms, J.M.J. Fréchet, Adv. Synth. Catal. 348 (2006) 1125.
[13] A. Dahan, M. Portnoy, J. Polym. Sci. A. Polym. Chem. 43 (2005) 235.
[14] R. van de Coevering, R.J.M. Klein Gebbink, G. van Koten, Prog. Polym. Sci. 30 (2005) 474.
[15] R. van Heerbeek, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.N.H. Reek, Chem. Rev. 102 (2002) 3717.
[16] B. Romagnoli, W. Hayes, J. Mater. Chem. 12 (2002) 767.
[17] O. Herd, A. Hessler, M. Hingst, M. Tepper, O. Stelzer, J. Organomet. Chem. 522 (1996) 69.
[18] I. Angurell, G. Muller, M. Rocamora, O. Rossell, M. Seco, Dalton Trans. (2003) 1194.

[19] M.L. Lartigue, M. Slany, A.M. Caminade, J.P. Majoral, Chem. Eur. J. 2 (1996) 1417.
[20] M. Slany, A.M. Caminade, J.P. Majoral, Tetrahedron Lett. 37 (1996) 9053.
[21] I. Angurell, G. Muller, M. Rocamora, O. Rossell, M. Seco, Dalton Trans. (2004) 2450.
[22] D.C. Tully, J.M.J. Fréchet, Chem. Commun. (2001) 1229.