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Synthesis and structural characterization of carbosilane ruthenium(II) metallodendrons containing cymene units

Marta Maroto-Diaz [a], Natalia Sanz del Olmo [a, b, c], Sandra Garcia-Gallego [a, c], Rafael Gómez [a, b, c], Paula Ortega [a, b, c, **], F. Javier de la Mata [a, b, c, *]

[a] Department of Organic and Inorganic Chemistry, And Research Institute in Chemistry "Andrés M. Del Río" (IQAR), University of Alcalá, Madrid, Spain
[b] Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Spain
[c] Institute Ramón y Cajal for Health Research (IRYCIS), IRYCIS, Spain

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ABSTRACT

The development of heterofunctional carbosilane dendrons with Schiff base ligands in the focal point and allyl or dimethylamino groups in their periphery was achieved. The presence of donor atoms with coordinative capacity enabled the synthesis of ruthenium(II) metallodendrons with cymene units. Depending on the Schiff base ligand present at the focal point of the dendrons, the functionalization of these systems with dimethylamino groups improved the solubility with respect to their analogues with allyl groups, obtaining systems soluble in aqueous medium. The presence of chelate ligands enhanced the stability of the final compounds.This discovery is a starting point to accomplish stable metallodendrons that in future could be tested as possible anticancer agents.

1. Introduction

In the last three decades there has been a multitude of research on the synthesis, characterisation and uses of dendritic systems [1–5]. According to their topology, the monodisperse dendritic systems can be classified into spherical; conical, also called dendrons or dendritic wedges and Janus dendrimers. This type of compounds has attracted the attention of both basic research and research oriented to technological applications mainly due to the possibility of locating many close functional groups, which can later be modified [6–10]. In recent years, the complexity of dendritic systems has exponentially increased, in response to the growing demand for multifunctional materials. Among the family of heterofunctional dendritic molecules, [11–13], dendrons have emerged as the simplest strategy towards monodisperse entities. They exhibit a desired moiety in the focal point and other different ones at the periphery, developed in a controlled process. Furthermore, linking two dendrons with different peripheral groups, topologies or generations, led to the so-called Janus-type dendrimers. Gradually, their relevance has increased due to their versatile behaviour including their use in self-assembly processes, [14,15], the possibility of precisely introducing desired molecules at the focal point [16–18] or surface, [19], and even in the modification of a multitude of materials [20,21].

The incorporation of metal atoms in the dendritic scaffold – generating the so-called metallodendrimers-is a successful strategy to combine the typical properties of transition metals (optical, catalytic, electrochemical, magnetic, etc.) [22–25] and the advantages of dendritic macromolecules (permeability, recyclability, isolation, etc.) [5]. The choice of the metal determines the subsequent application of the dendritic system. Surprisingly, few examples of metal-containing dendrons can be found in the bibliography. Relevant examples include Fréchet-type dendrons functionalized with nickel(II) or palladium (II) complexes at the

* Corresponding author. Department of Organic and Inorganic Chemistry, University of Alcala, UAH Campus. Faculty of Pharmacy, 28871, Alcalá de Henares, Spain.
** Corresponding author. Department of Organic and Inorganic Chemistry, and Research Institute in Chemistry "Andrés M. Del Río" (IQAR), University of Alcalá, Madrid, Spain.
E-mail addresses: paula.ortega@uah.es (P. Ortega), javier.delamata@uah.es (F.J. de la Mata).

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focal point, used as catalysts in polymerization processes [26,27]. In the biomedical field, ferrocene-containing carbosilane dendrons have been reported, with antibacterial properties [28] or the poly(arylether) or poly(amidoamine) metallodendrons with anticancer activity have been reported [29,30].

Our experience in the field of carbosilane dendritic and metallodendritic systems and their application in biomedicine [31–33] encouraged us to pursue new heterofunctional systems with improved activities. We have recently reported the synthesis of ruthenium(II) η^6-*p*-cymene-based spherical carbosilane dendrimers, which are cytotoxic towards cisplatin-resistant tumour cell lines [34,35]. Herein, we explored the possibility of designing heterofunctional carbosilane dendrons in a controlled way, that contain organometallic Ru(II) η^6-*p*-cymene complexed to Schiff base ligands [36] at the focal point and multiple cationic charges on the surface in order to improve the solubility of these systems in water or physiological medium. We evaluated their stability in protic solvents in order to determine their future applications.

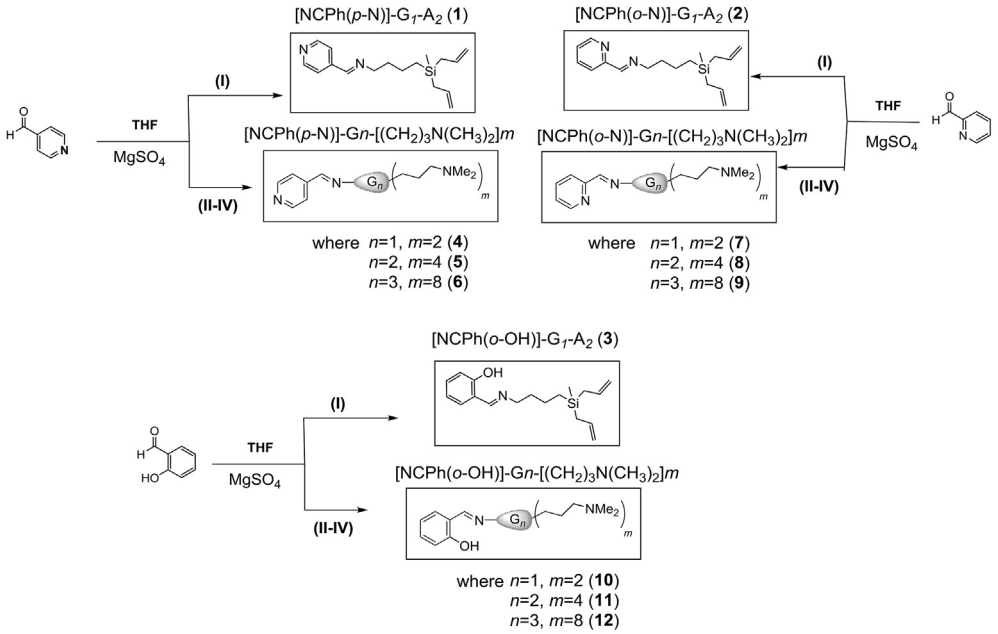
2. Results and discussion

The new heterofunctional metallodendrons were synthesized using a similar two-step strategy to that described for spherical carbosilane dendrimers [35]. In the first step, the precursor dendrons NH_2-G_n-$(Ally)_m$ and NH_2-G_n-$(NMe_2)_m$ previously described in the bibliography [37] (G_n indicates the dendrimer generation and m determines the number of functional groups on the surface) were reacted with different aldehydes through Schiff-base condensation reactions to deliver *N*-monodentade, *N,N*-chelating and *N,O*-chelating species in the focal point. The versatility of these dendritic materials relies on the different peripheral functionalization, with allyl or -NMe_2 groups, which can tune the solubility of the overall dendron, as well as the variety of metal complexes that can be coordinated at the focal point, improving the anticancer activity. As proof-of-concept, in the second step, [Ru(η [6]-*p*-cymene)] complexes were attached to the focal point.

2.1. Synthesis and structural characterization of dendrons with Schiff base at the focal point and allyl or $-N(NMe_2)_2$ groups at the periphery

The strategy to accomplish Schiff-base-containing carbosilane dendrons **1**–**12** relied on the condensation reaction between the primary amine in the precursor dendron and an aldehyde in the presence of $MgSO_4$ as drying agent. The allyl-functional dendrons [NCPh(*p*-N)]-G_1-A_2 (**1**); [NCPh(*o*-N)]-G_1-A_2 (**2**) and [NCPh(*o*-OH)]-G_1-A_2 (**3**) were synthesized through the reaction of the first-generation precursor NH_2-G_1-A_2 (**I**) with the corresponding aldehyde: 4-pyridinecarboxaldehyde for **1**; 2-pyridinecarboxaldehyde for **2** and salicylaldehyde for **3** in the presence of $MgSO_4$ and using THF as solvent at room temperature (Scheme 1). An analogous procedure was used to react the precursor dendrons NH_2-G_n-$[(CH_2)_3N(Me)_2]_m$ of several generations ($n = 1$, $m = 2$ (**II**); $n = 2$, $m = 4$ (**III**); $n = 3$, $m = 8$ (**IV**)) [38,39] with slight excess of the corresponding aldehyde, in order to obtain the *N*-monodentate [NCPh(*p*-N)]-G_n-$[(CH_2)_3N(CH_3)_2]_m$ ($n = 1$, $m = 2$ (**4**); $n = 2$, $m = 4$ (**5**); $n = 3$, $m = 8$ (**6**)); *N,N*-chelating [NCPh(*o*-N)]-G_n-$[(CH_2)_3N(CH_3)_2]_m$ ($n = 1$, $m = 2$ (**7**); $n = 2$, $m = 4$ (**8**); $n = 3$, $m = 8$ (**9**)) and *N,O*-chelating imine [NCPh(*o*-OH)]-G_n-$[(CH_2)_3N(CH_3)_2]_m$ ($n = 1$, $m = 2$ (**10**); $n = 2$, $m = 4$ (**11**); $n = 3$, $m = 8$ (**12**)) dendrons (Scheme 1). Compounds **1-12** were obtained as brown or yellow oils after purification by size exclusion chromatography using THF as eluent. Dendrons **1-12** are soluble in organic solvents, including DMSO, insoluble in water.

The presence of the new aldimine fragment corresponding to the new CH═N group formed by Schiff-condensation reaction was confirmed by ^{1}H and ^{13}C- NMR [40] through the existence of a new signal at a chemical shift of 8.23 (s) and 158.8 ppm for **1-4**; 8.31 (s) and 161.7 ppm for **5**–**8**; and 8.32 (s) and 164.6 ppm **9**–**12** respectively. Furthermore, the aldimine group induces a strong deshielding on the methylene group directly linked to the nitrogen atom displacing the resonance from 2.60 ppm in ^{1}H NMR spectrum for the precursors, up to approximately 3.60 ppm for the final products. This same effect was observed in ^{13}C-{^{1}H} NMR,



Scheme 1. Synthesis of carbosilane dendrons **1-12**.

observing the new signal around 59.2–61.6 ppm for the new derivatives **1**–**12**. The aromatic ring directly bound to the aldimine moiety appears, in the ^{1}H- and ^{13}C-{^{1}H} NMR spectra, as a set of signals with a distribution according to a AA'BB'-type spin system in the case of the pyridine ligand with nitrogen in *para* position (**1,4-6**), and a ABCD-type spin system in the case of the pyridine (**2, 7-9**) and phenol (**3, 10-12**) ligands with the heteroatom in *ortho* position. In the specific case of the dendrons with a phenol group at the focal point (**3, 10-12**), the broad singlet around 13.65 ppm was assigned to the proton of the hydroxyl group.

Two-dimensional {^{1}H-^{15}N} HMBC experiments also confirmed the formation of an imine-type bond C=N at the dendrons focal point. Compounds **1, 2** and **4-9** revealed two new signals at −64.5 and −37.3 ppm assigned to the pyridineimine group, while compounds **3** and **10-12** exhibited a single signal at −82.5 ppm due to the phenolimine moiety. The rest of signals in the spectra, corresponding to the carbosilane scaffold, were consistent with those reported in bibliography [38].

The ESI-TOF-POS mass spectra showed the peaks corresponding to the molecular ion $[M+H]^{+}$ of the dendritic compounds **1** and **2** ($m/z = 287.19$ uma), **4** and **7** ($m/z = 577.42$ uma), **3** ($m/z = 302.19$ uma) and **10** ($m/z = 592.44$ uma). However, it was not possible to detect the molecular peak of second- and third-generation derivatives.

2.2. Synthesis and structural characterization of ruthenium(II) metallodendrons

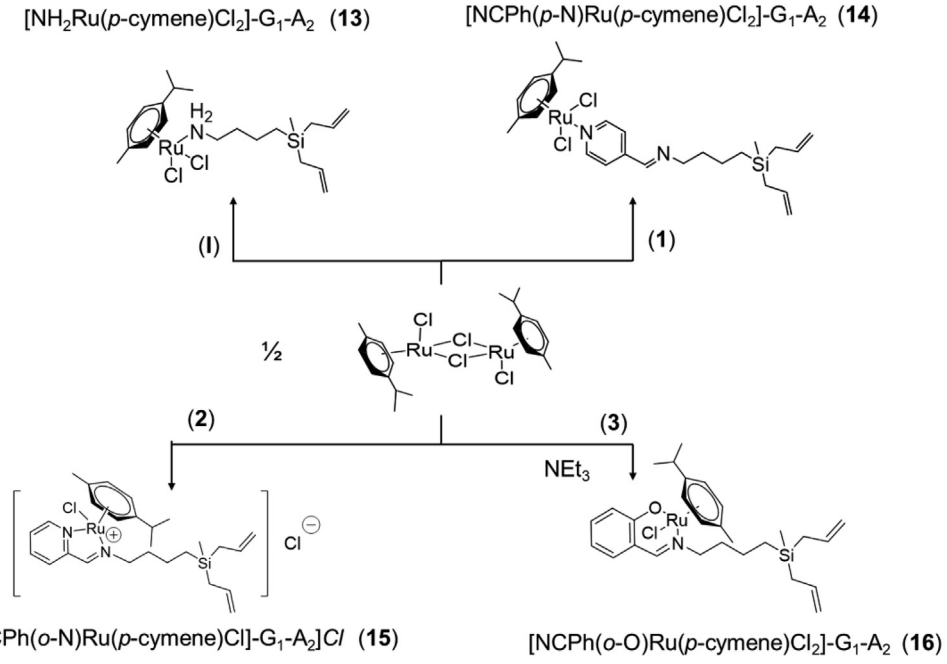
The metal complexation capacity of dendrons **1**–**12** was evaluated using the ruthenium(II) derivative [Ru(η^{6}-*p*-cymene)Cl$_2$]$_2$. Different heterofunctional dendrons were accomplished, functionalized with allyl or -N(CH$_2$)$_3$ groups in the periphery, and with *N*-monodentate or *N,N*- or *N,O*-chelate type coordination complexes at the focal point depending on the nature of the donor atoms present in the precursor dendrons. It is worth mentioning that the metal complexation step was performed using an stoichiometric ratio between the corresponding dendron and Ru(II) ion, *i.e.* dendron: [Ru(η^{6}-*p*-cymene)Cl$_2$]$_2$ molar ratio 1:0.5.

2.2.1. Metallodendrons functionalized with allyl groups on the surface

The bridge-splitting reaction of the [Ru(η^{6}-*p*-cymene)Cl$_2$]$_2$ with the dendritic ligands **I**, **1**, **2** and **3** generated a *N*-monodentate, *N,N*- or *N,O*-chelating imine ruthenium complex into the focal point using a similar procedure to that previously reported [35]. This synthetic strategy led to metallodendrons [Cl$_2$(η^{6}-*p*-cymene)RuNH$_2$]-G$_1$-A$_2$ (**13**), [Cl$_2$(η^{6}-*p*-cymene)RuNCPh(*p*-N)]-G$_1$-A$_2$ (**14**), [[Cl(η^{6}-*p*-cymene)RuNCPh(*o*-N)]-G$_1$-A$_2$]Cl (**15**) and [Cl(η^{6}-*p*-cymene)RuNCPh(*o*-O)]-G$_1$-A$_2$ (**16**) exhibiting allyl groups at the periphery (Scheme 2). Compounds **13, 14** and **16** were brown oils, soluble in organic solvents, including DMSO, but insoluble in water, while **15** is a brown oil soluble in water and DMSO due to its cationic nature.

All new metallodendrons were characterized by ^{1}H,^{13}C-{^{1}H}, ^{29}Si-NMR, elemental analysis and ESI-TOF (see experimental part for more details). The Ru(II) complexation was confirmed through ^{1}H and ^{13}C-{^{1}H}NMR (Fig. 1), where the signal assigned to the methylene or methinic group closest to the nitrogen atom in the dendron is shifted towards high frequency region after metal coordination (see Table 1 and Fig. 1). The metal complexation also shifted the signals assigned to the methinic groups in the aromatic fragments, although to a lower extent, but did not affect the resonances corresponding to the methylene and methyl groups of the carbosilane scaffold.

An exhaustive analysis of the aromatic region in the ^{1}H and ^{13}C-{^{1}H}-NMR spectra shown relevant information regarding the coordination mode in the new metallodendrons **13**–**16**. The presence of two pseudo-doublets at 5.24 and 5.42 ppm in ^{1}H NMR spectra assigned to the CH$_{cym}$ groups in the *p*-cymene ring and two unique signals in the range 80.5–83.2 ppm in ^{13}C-{^{1}H} spectra (Fig. 1.A-B) confirm the existence of a symmetry plane in the structure of the neutral metallodendrons **13** and **14** and revealed a *N*-monodentate coordination. Conversely, as a consequence of the new chiral environment of the metal atom in compounds **15** and **16**, the symmetry plane could be not observed. In these cases, the resonances of four non-equivalent CH$_{cym}$ groups were observed as multiplets at δ 5.04–6.22 and δ 80.2–87.1 ppm in ^{1}H and ^{13}C NMR respectively (Fig. 1.C-D).



Scheme 2. Synthesis of allyl-functional Ru(II) metallodendrons **13-16**.

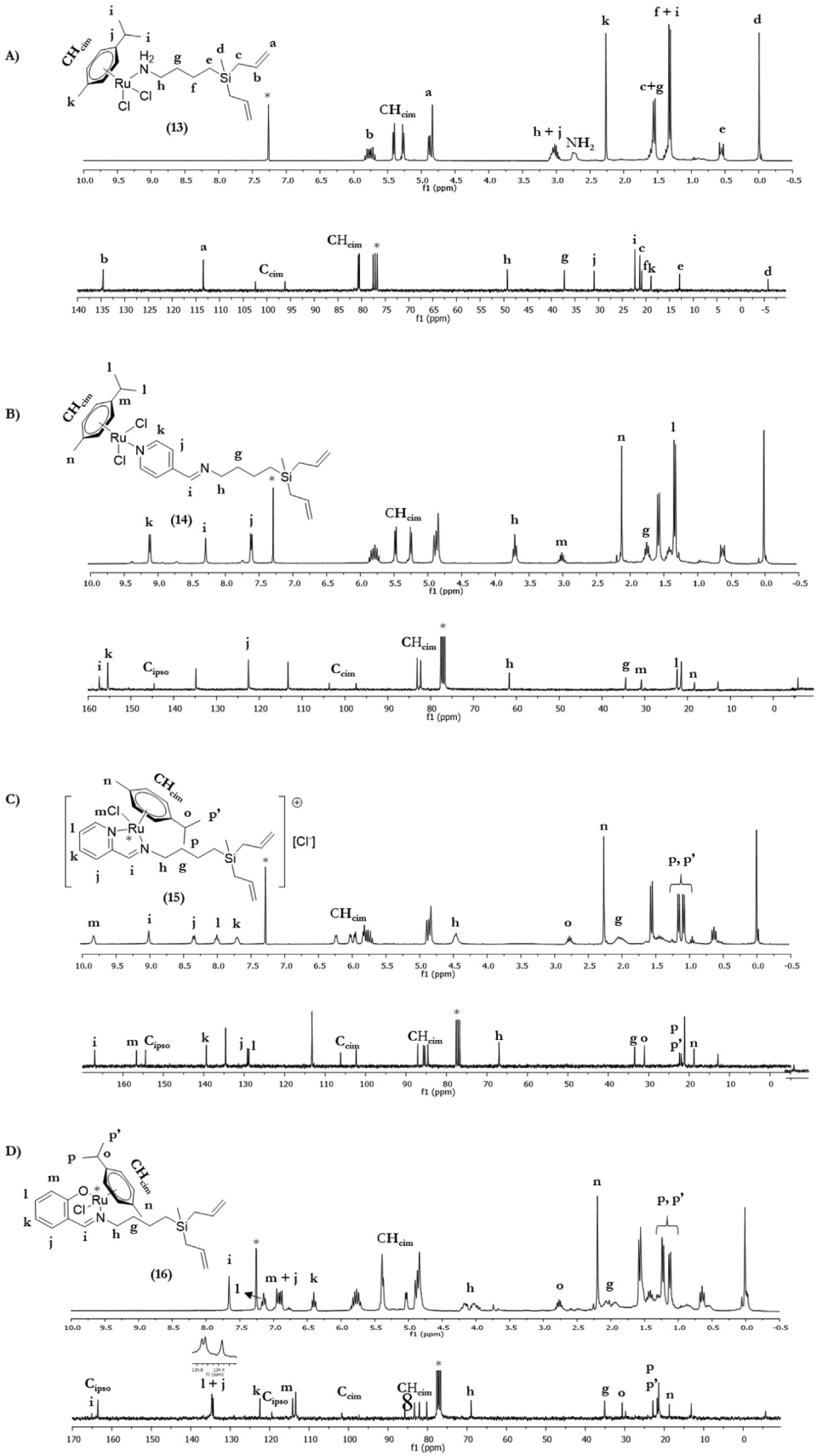


Fig. 1. ^{1}H NMR and ^{13}C-{^{1}H} spectra of [Cl_2(η^6-*p*-cymene)RuNH_2]-G_1-A_2 (**13**), [Cl_2(η^6-*p*-cymene)RuNCPh(*p*-N)]-G_1-A_2 (**14**), [[Cl(η^6-*p*-cymene)RuNCPh(*o*-N)]-G_1-A_2]Cl (**15**) and [Cl(η^6-*p*-cymene)RuNCPh(*o*-O)]-G_1-A_2 (**16**) in $CDCl_3$ (*).

Table 1
Selected data of chemical Shift of CH_2N in compounds **13**–**16** (dendrons and metallodendrons named as MTD) using $CDCl_3$ as a solvent.

		^{1}H NMR(ppm)		^{13}C{H}-NMR(ppm)	
Metallodendron	Group	dendron	MTD*	dendron	MTD*
13	$-CH_{2(h)}N$	2.60	3.02	41.7	49.3
14	$-CH_{2(k)}N$	8.67	9.09	150.5	155.4
15	$-CH_{2(h)}N$	3.65	4.43	61.3	67.0
	$-CH_{2(m)}N$	8.63	9.81	149.5	156.7
16	$-CH_{2(h)}N$	3.56	4.08	59.2	69.2

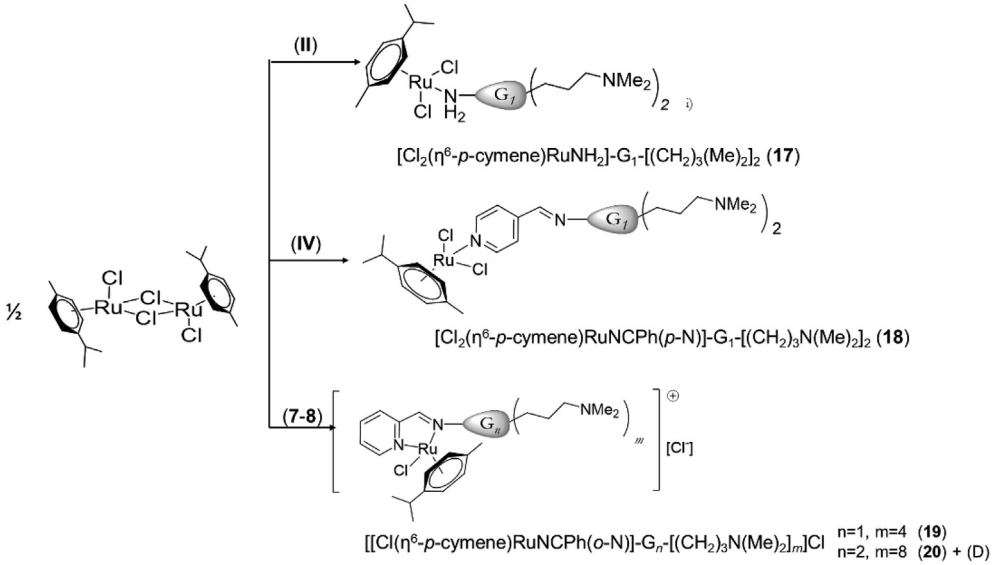
*MTD: metallodendron.

2.2.2. Metallodendrons functionalized with -N(Me)$_2$ groups at the periphery

The synthesis of the first-generation derivatives [$Cl_2(\eta^6$-*p*-cymene)RuNH$_2$]-G$_1$-[$(CH_2)_3N(Me)_2]_2$ (**17**) and [$Cl_2(\eta^6$-*p*-cymene)RuNCPh(*p*-N)]-G$_1$-[$(CH_2)_3N(Me)_2]_2$ (**18**) from the ligands [NH_2]-G$_1$-[$(CH_2)_3N(Me)_2]_2$ (**II**) and [NCPh(*p*-N)]-G$_1$-[$(CH_2)_3N(Me)_2]_2$ (**4**), respectively, was carried out by the general procedure previously described for the *N*-monodentate systems (Scheme 3). Unfortunately, the poor stability of these systems over time hindered the isolation of higher generation analogues. The ^{1}H and ^{13}C-{^{1}H} NMR spectra of compounds **17** and **18** confirmed the exclusive metal complexation at the focal point, ruling out any Ru(II) coordination to peripheral NMe_2 groups (Fig. 2). Again, no chemical shift changes were observed for carbosilane scaffold signals.

Aiming for higher stability metallodendrons, *N,N*-chelate complexes were explored. First-generation metallodendron [[Cl(η^6-*p*-cymene)RuNCPh(*o*-N)]-G$_1$-[$(CH_2)_3N(Me)_2]_2$]Cl (**19**) was detected as a single product in ^{1}H and ^{13}C-{1H} NMR spectra, when the reactions were carried out in methanol. The formation of second-generation analogue [[Cl(η^6-*p*-cymene)RuNCPh(*o*-N)]-G$_2$-[$(CH_2)_3N(Me)_2]_4$]Cl (**20**) could be detected in ^{1}H NMR spectra in CD_3OD under selected experimental conditions, but also the presence of [{(η^6-*p*-cymene)Ru}$_2(\mu$-$OCH_3)_3]^+$ species (**D**) [41,42].

In order to gain further insight into the formation of compound **D**, a series of experiments were carried out (Fig. 3). In a first assay, we aimed to establish the influence of the temperature when the reaction was carried out in a protic solvent such as CD_3OD (Fig. 3.B vs 3.C). The experiment confirmed that the formation of **D** decreases at low temperature (−78 °C). In a second assay, we wanted to clarify the role of the tertiary amines present in the dendritic systems. Accordingly, we monitored the reaction in CD_3OD of the ruthenium dimer [Ru(η^6-*p*-cymene)$Cl_2]_2$ with $Et_3Si(CH_2)_3NMe_2$- **V** (*reaction* 1, Fig. 4.C), as well as with first-generation carbosilane dendrimer G$_1$-[$SiMe_2(CH_2)_3$ NMe_2]$_4$ **VI** [32] (*reaction* 2, Fig. 4.E), functionalized with one and four $N(CH_3)_2$ groups respectively but keeping 1:4 ratio for [Ru]:[-$N(CH_3)_2$] in both cases (Fig. 4). This experiment showed that the absence of a bidentate *N*-type, *N*-chelate ligand in the structure of dendrimers **V** and **VI** led to a complete transformation of the initial ruthenium complex [Ru(η^6-*p*-cymene)$Cl_2]_2$ to compound **D**. Furthermore, ^{1}H signals assigned to -$N(Me)_2$ groups shifted towards higher frequency with respect to the dendritic precursors, revealing the potential participation of these amines in the formation of **D** species. Compound **D** was also obtained through the reaction with four equivalents of the tertiary amine $RN(Me)_2$ (R = $Et_3Si(CH_2)_3$). In all experiments, the *p*-cymene ring in species **D** was an achiral nature, for that, in the beginning, these characteristic signs of the new species seem to be related to the presence in their structure of a *p*-cymene ring with a spin system of type AA'BB'. In addition to the appearance of two pseudo-doublets in the ^{1}H NMR spectrum at a chemical shift of 5.23 and 5.42 ppm, a multiplet at 2.79 ppm corresponding to the CH of the isopropyl group was also observed, as well as a single doublet ($^3J_{(HH)}$ = 6.9 Hz) at a frequency of 1.27 ppm due to the presence of two equivalent methyl groups in the ring (Fig. 4C and E). So this distribution of signals would support a coordination of *N*-monodentate type or the existence of a plane of



Scheme 3. Synthesis of metallodendrons **17** and **18** (Experimental conditions: 2 h, CH_2Cl_2, r.t.) and **19** (Experimental conditions: 3 h, methanol, r.t.).

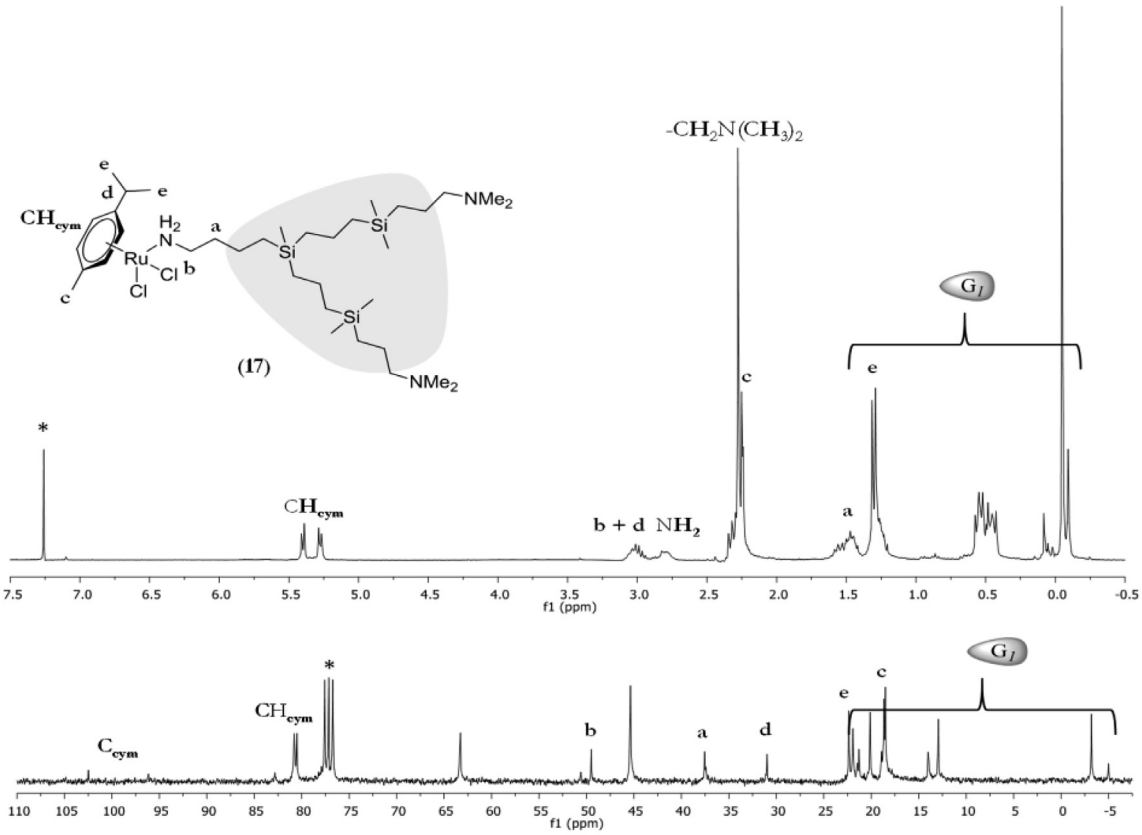


Fig. 2. ^{1}H and ^{13}C-{^{1}H} NMR spectra of $[Cl_2(\eta^6$-*p*-cymene)$RuNH_2]$-G_1-$[(CH_2)_3N(NMe)_2]_2$ (**17**) in $CDCl_3$ (*).

symmetry in the structure. Finally, using the products obtained in *Reactions 1* and *2*, two types of complementary assays were carried out which enabled the identification of the structure and composition of the **D** species. On the one hand, the Mass Spectrometry assay revealed two molecular peaks for the products from *Reaction 1*: 202.19 uma, attributed to the molecular peak $[M + H]^+$ of the ligand **V**, and 565.09 uma, with a characteristic isotopic distribution of ruthenium (Fig. S14). On the other hand, DOSY-2D diffusion experiments on the *Reaction 2* products mixture compared to the precursor dimer, confirmed the dinuclear nature of **D** and ruled out the coordination of the fragment $[Ru(\eta^6$-*p*-cymene)] to the peripheral amines of the carbosilane dendrimer **VI**. That is, **D** and **VI** were independent species (Fig. S15).

Therefore and in view of the results obtained in these experiments, **D** species was assigned to the compound $[\{(\eta^6$-*p*-cymene)$Ru\}_2(\mu$-$OCH_3)_3]^+$ previously described by some authors [43,44]. The proposed mechanism towards the formation of **D** may be related to an acid-based reaction between the alcoholic solvent and the dimethylamine groups favored by the presence of the ruthenium(II) complex $[Ru(\eta^6$-*p*-cymene$)Cl_2]_2$ (Scheme S1).

Given the drawbacks associated with the use of a protic solvent in this type of reaction, carrying out the synthetic procedure in chloroform finally resulted in the production of the second-generation metallodendron **20** as a single product. Unfortunately, the metallodendron instability was manifested through the release of the *p*-cymene ligand over time, in addition to other decomposition products that could not be identified. The expected instability that Ru(II) complexes present when the dendron contains amino groups on the surface discouraged us of pursuing the preparation of the corresponding derivates from *N,O*- chelate systems and NMe_2 amines (**10**–**12**) and the third generation dendron **9**.

3. Conclusions

A successful synthetic protocol for the preparation of a series of dendrons functionalized at the focal point with *N*-monodentate ligands, or *N,N*- or *N,O*-chelate-type ligands have been achieved. These dendrons allow the synthesis of different heterofunctional metallodendrons comprising a focal $[Ru(\eta^6$-*p*-cymene)] fragment and peripheral allyl or amine -$N(Me)_2$ groups that can be achiral or quiral depending on the ligand used. It has been shown that the stability of the final metallodendrons depends on several factors: (i) the nature of the peripheral functional groups, (ii) the generation or number of peripheral groups, and iii) the solvent used in the preparation reaction.

Allyl-functional dendrons can be modified to display *N*-monodentate, *N,N*- or *N,O*-chelate at the focal point, being perfectly stable in organic solvents, such as DMSO that could be used for biomedical experiments when its presence is lower than 0.6%. Accordingly, these metallodendrons can be considered as prodrugs of active species and could be explored in the future as anticancer agents. Conversely, the presence of NMe_2 units in the dendritic surface enhanced the solubility of these compounds in aqueous medium and could provide new applications for these derivatives. Nevertheless, metallodendrons comprising a *N*-monodentate fragment at the focal point revealed poor stability *via* release of cymene ligands as well as non-identifiable species, and prevented he preparation of higher generation analogues. The presence of *N,N*-chelate fragments in the focal point led to Ru(II) metallodendrons whose formation and stability depend on the generation and the type of solvent used. In protic medium, such as alcohols, it is only possible to isolate the first-generation compounds, since an excess of amino groups led to the formation of the

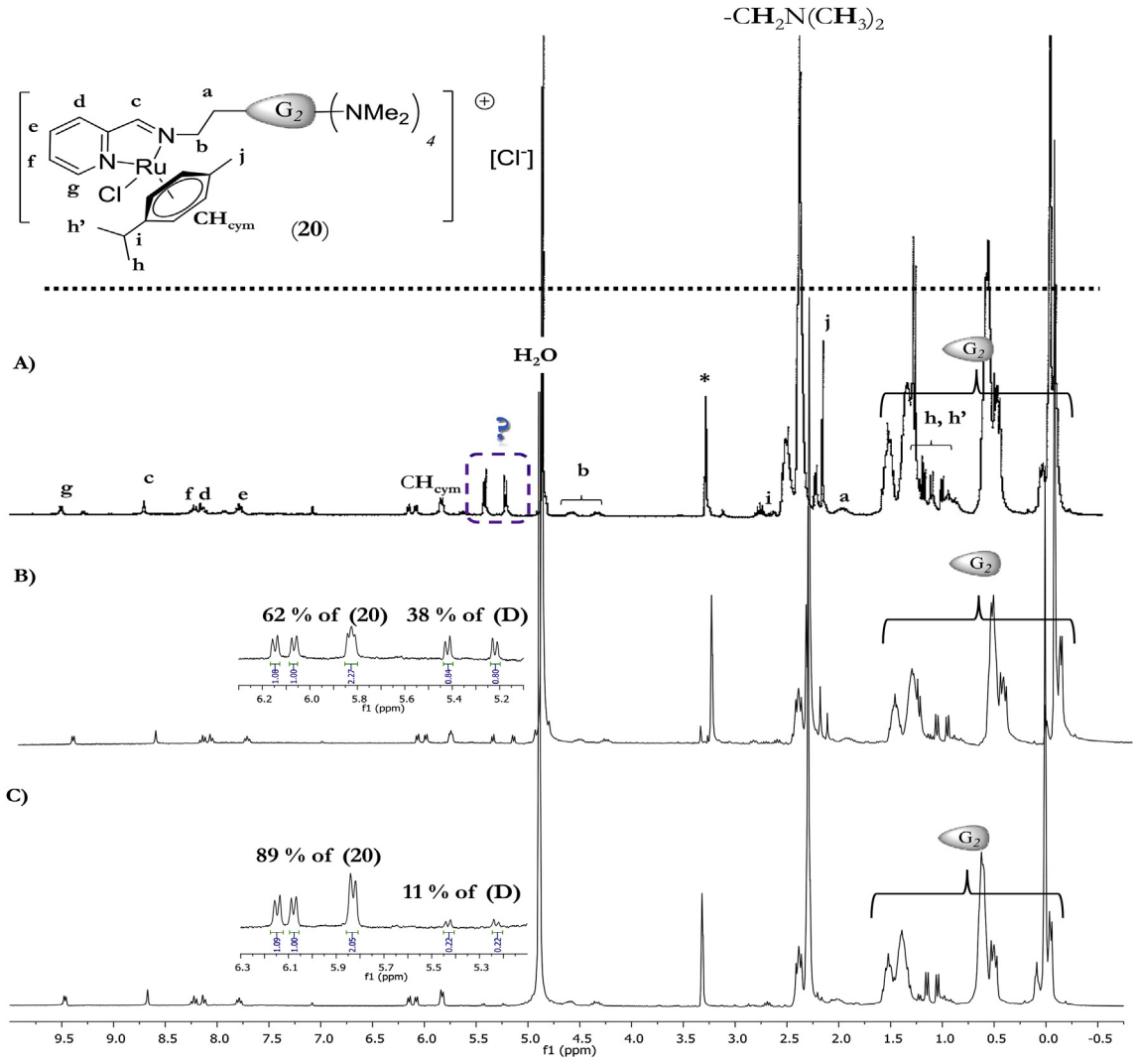


Fig. 3. ^{1}H NMR spectra of the reaction between the dendritic ligand [NCPh(*o*-N)]-G_2-[$(CH_2)_3N(CH_3)_2$]$_4$ (**8**) and ½ [Ru(η^6-*p*-cymene)Cl_2]$_2$ in A) ethanol, r.t.; B) methanol, r.t.; C) methanol, −78 °C.

derivative [{(η^6-*p*-cymene)Ru}$_2$(μ-OCH_3)$_3$]$^+$. In non-protic solvent, the desired derivative is formed regardless of generation.

4. Methods

4.1. General considerations

Solvents were purified from appropriate drying agents when necessary. Unless otherwise specified, the chemicals were purchased from commercial sources and used as received. *Elemental analysis*. The quantitative analysis of carbon, hydrogen and nitrogen of the described derivatives were carried out in a LECO CHNS-932 microanalyzer. *Nuclear magnetic resonance*. ^{1}H, ^{13}C and ^{31}P NMR assays were performed on Varian spectrometers Unity-300 and Mercury-300. Two-dimensional spectra HSQC {^{1}H-^{13}C}, HMBC {^{1}H-^{29}Si}, HMBC{^{1}H-^{15}N}, TOCSY and DOSY-2D diffusion experiments were performed at 25 °C in a Bruker AV400 or Unity-500 spectrometer. The chemical shifts (ppm) were measured relative to the residual signal of ^{1}H and ^{13}C of the deuterated solvents, in the spectra of ^{29}Si tetramethylsilane (TMS) was taken as reference and in those of ^{15}N nitromethane (CH_3NO_2).*Mass spectrometry*. The different compounds were analyzed by means of the ionization technique ESI-TOF-POS in a Bruker Ultraflex III instrument. Reflector mode registrations were made from 450 to 5000 uma.

4.2. General synthetic chemical procedures

4.2.1. Synthesis of [NCPh(p-N)]-G_1-A_2 (1)

To a THF solution containing the precursor with an NH_2 group at the focal point (**I**) (102 mg, 0.52 mmol), 4-pyridinecarboxaldehyde (55.3 mg, 0.50 mmol) was added. The reaction mixture was maintained under constant stirring at room temperature and in the presence of $MgSO_4$ for 12 h. After completion of the reaction, the solution was evaporated to dryness and the crude reaction was purified by extraction CH_2Cl_2/H_2O (1:1), obtaining compound **1** as a yellow oil (132.1 mg, 89%). $C_{17}H_{26}N_2Si$ (286.49 g/mol). **^{1}H-NMR ($CDCl_3$):** δ −0.02 (s, 3H, -$CH_2Si(CH_3)(CH_2)_2$); 0.60 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 1.38 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 1.54 (m, 4H, -$CH_2Si(CH_3)(CH_2)_2$); 1.72 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 3.65 (t, $^{3}J_{(H\text{-}H)}$ = 6.9 Hz, 2H, -$NCH_2CH_2CH_2CH_2Si$); 4.83 (m, 4H, -$Si(CH_2CHCH_2)_2$); 5.75 (m, 2H, -$Si(CH_2CHCH_2)_2$); 7.57 (m, 2H, Ar); 8.67 (m, 2H, Ar); 8.25 (s, 1H, -CH_{imine}). **^{13}C {^{1}H}-NMR ($CDCl_3$):** δ −5.7 (-$CH_2Si(CH_3)(CH_2)_2$); 12.9 (-$NCH_2CH_2CH_2CH_2Si$); 21.3 (-$NCH_2CH_2CH_2CH_2Si$); 21.4 (-$CH_2Si(CH_3)(CH_2)_2$); 34.5

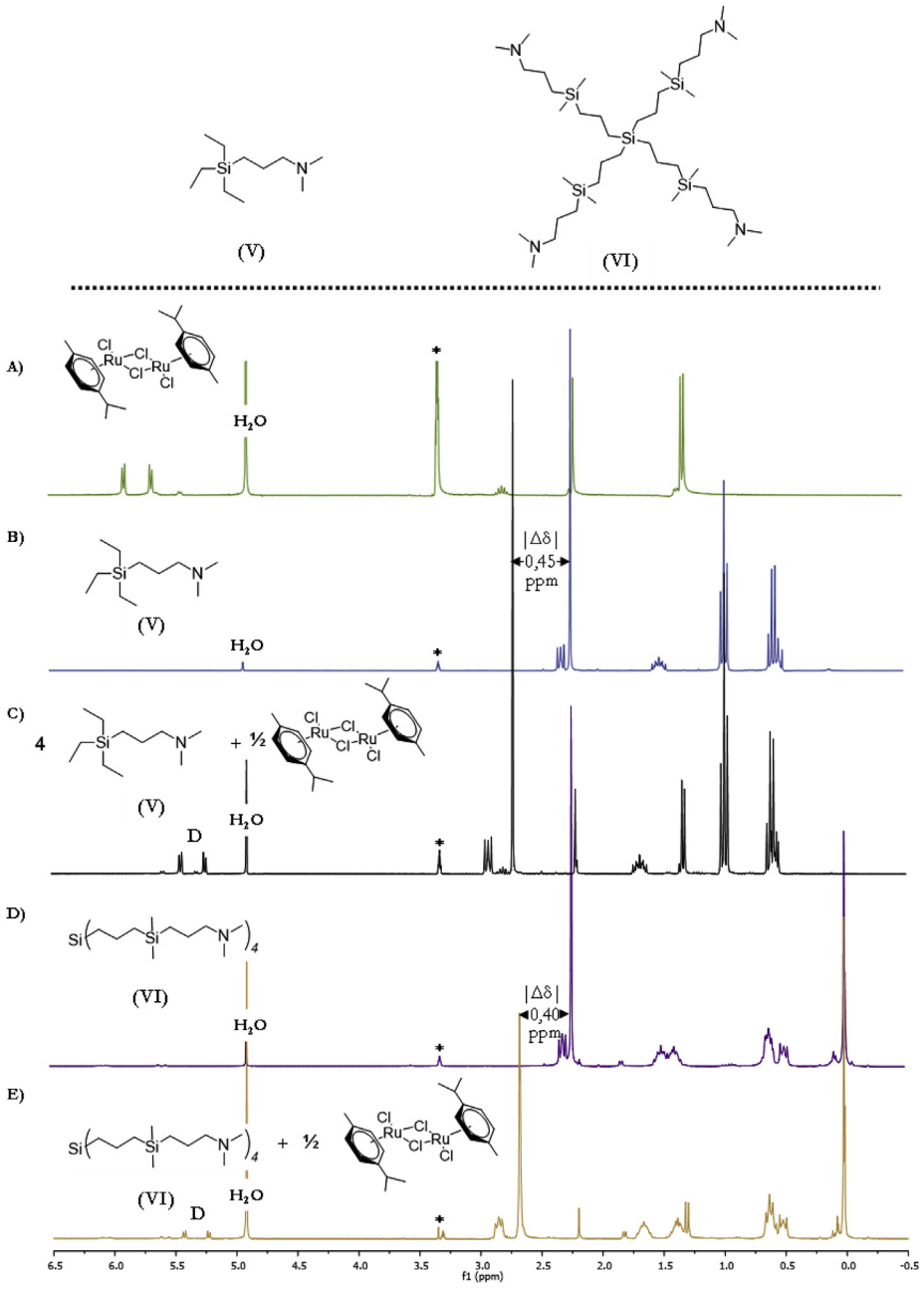


Fig. 4. ^{1}H NMR spectra in CD_3OD(*) of A) [Ru(η^6-*p*-cymene)Cl_2]$_2$; B) mononuclear model **V**; C) **V** with ½ eq. [Ru(η^6-*p*-cymene)Cl_2]$_2$; D) dendrimer **VI**; E) **VI** with ½ eq. [Ru(η^6-*p*-cymene)Cl_2]$_2$.

(-NCH$_2$*C*H$_2$CH$_2$CH$_2$Si); 61.6 (-N*C*H$_2$CH$_2$CH$_2$CH$_2$Si); 113.3 (-Si(CH$_2$*C*HCH$_2$)$_2$); 134.8 (-Si(CH$_2$*C*HCH$_2$)$_2$); 122.0, 143.2, 150.5 (*C*$_{Ar}$); 159.0 (-*C*H$_{imine}$). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-CH$_2$*Si*(CH$_3$)(CH$_2$)$_2$). **^{15}N-NMR ($CDCl_3$):** δ −64.5 (-*N*$_{pir}$); −32.0 (-*N*$_{imine}$).**Elemental Analysis (%):** Calc. C, 71.27; H, 9.15; N, 9.78; Exp.: C, 70.61; H, 9.46; N, 9.48. **MS:** $[M+H]^+ = 287.19$ uma.

4.2.2. Synthesis of [NCPh(o-N)]-G_1-A_2 (2)

The first generation dendron (**2**) was prepared and purified following the same procedure as for compound **1**, using the following reagents: NH_2-G_1-A_2 (98.3 mg, 0.50 mmol) and 2-pyridinecarboxaldehyde (53.1 mg, 0.50 mmol). Compound **2** was isolated as a yellow oil (114.5 mg, 77%). **^{1}H-NMR ($CDCl_3$):** 0.03 (s, 3H, -CH$_2$Si(*CH*$_3$)(CH$_2$)$_2$); 0.59 (m, 2H, -NCH$_2$CH$_2$CH$_2$*CH*$_2$Si); 1.39 (m, 2H, -NCH$_2$CH$_2$*CH*$_2$CH$_2$Si); 1.52 (m, 4H, -CH$_2$Si(CH$_3$)(*CH*$_2$)$_2$); 1.73 (m, 2H, -NCH$_2$*CH*$_2$CH$_2$CH$_2$Si); 3.65 (t, $^{3}J_{(H-H)} = 6.9$ Hz, 2H, -N*CH*$_2$CH$_2$CH$_2$CH$_2$Si); 4.79 (m, 4H, -Si(CH$_2$CH*CH*$_2$)$_2$); 5.73 (m, 2H, -Si(CH$_2$*CH*CH$_2$)$_2$); 7.29 (m, 1H, Ar); 7.72 (m, 1H, Ar); 7.96 (m, 1H, Ar); 8.63 (m, 1H, Ar); 8.36 (s, 1H, -*CH*$_{imine}$). **^{13}C {^{1}H}-NMR ($CDCl_3$):** 5.7 (-CH$_2$Si(*CH*$_3$)(CH$_2$)$_2$); 12.9 (-NCH$_2$CH$_2$CH$_2$*CH*$_2$Si); 21.3 (-NCH$_2$CH$_2$*CH*$_2$CH$_2$Si); 21.4 (-CH$_2$Si(CH$_3$)(*CH*$_2$)$_2$); 34.5 (-NCH$_2$*CH*$_2$CH$_2$CH$_2$Si); 61.3 (-N*CH*$_2$CH$_2$CH$_2$CH$_2$Si); 113.2 (-Si(CH$_2$*CH*CH$_2$)$_2$); 134.8 (-Si(CH$_2$*CH*CH$_2$)$_2$); 121.3, 124.7, 136.6, 149.5, 155.0 (*C*$_{Ar}$); 161.8 (-*CH*$_{imine}$). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-CH$_2$*Si*(CH$_3$)(CH$_2$)$_2$). **^{15}N-NMR ($CDCl_3$):** δ −67.4 (-*N*$_{pir}$); −37.8 (-*N*$_{imine}$). **Elemental Analysis (%):** Calc. para $C_{17}H_{26}N_2Si$ (286.49 g/mol): C, 71.27; H, 9.15; N, 9.78; Exp.: C, 70.98; H, 8.72; N, 9.80. **MS:** $[M+H]^+ = 287.19$ uma.

4.2.3. Synthesis of [NCPh(o-OH)]-G_1-A_2 (3)

The compound **3** was prepared and purified following the same procedure as for compound **1**, using the following reagents: NH_2-G_1-A_2 (62.7 mg, 0.31 mmol) and salicylaldehyde (38.7 mg, 0.31 mmol). Compound **3** was isolated as a yellow oil (87.4 mg, 91%). **^{1}H-NMR ($CDCl_3$):** 0.03 (s, 3H, -CH_2Si(CH_3)(CH_2)$_2$); 0.60 (m, 2H, -$NCH_2CH_2CH_2CH_2$Si); 1.41 (m, 2H, -$NCH_2CH_2CH_2CH_2$Si); 1.55 (m, 4H, -CH_2Si(CH_3)(CH_2)$_2$); 1.72 (m, 2H, -$NCH_2CH_2CH_2CH_2$Si); 3.59 (t, ^3J $_{(H\text{-}H)}$ = 6.9 Hz, 2H, -NC$H_2$$CH_2CH_2CH_2$Si); 4.84 (m, 4H, -Si($CH_2CHCH_2$)$_2$); 5.75 (m, 2H, -Si($CH_2CH$$CH_2$)$_2$); 6.86 (m, 1H, Ar); 6.95 (m, 1H, Ar); 7.26 (m, 2H, Ar); 8.33 (s, 1H, -CHimine); 13.62 (s broad, 1H, -OH). **^{13}C {^{1}H}-NMR ($CDCl_3$):** 5.7 (-CH_2Si(CH_3)(CH_2)$_2$); 12.8 (-$NCH_2CH_2CH_2CH_2$Si); 21.3 (-$NCH_2CH_2CH_2CH_2$Si); 21.4 (-CH_2Si(CH_3)(CH_2)$_2$); 34.5 (-$NCH_2CH_2CH_2CH_2$Si); 59.2 (-$NCH_2CH_2CH_2CH_2$Si); 113.3 (-Si(CH_2CHCH_2)$_2$); 134.8 (-Si(CH_2CHCH_2)$_2$); 117.1, 118.5, 118.9, 131.2, 132.1, 161.4 (C_{Ar}); 164.6 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.1 (-CH_2Si(CH_3)(CH_2)$_2$). **^{15}N-NMR ($CDCl_3$):** δ −82.2 (-N_{imine}). **Elemental analysis (%):** Calc. $C_{18}H_{27}NOSi$ (301.51 g/mol): C, 71.71; H, 9.03; N, 4.65; Exp.: C, 71.36; H, 8.96; N, 5.08. **MS:** $[M+H]^+ = 302.19$ uma.

4.2.4. Synthesis of [NCPh(p-N)]-G_1-[$(CH_2)_3N(CH_3)_2]_2$ (4)

The first generation dendron (**4**) was prepared following the same procedure as for compound **1**, using the following reagents: NH_2-G_1-$[(CH_2)_3N(CH_3)_2]_2$ (386.4 mg, 0.79 mmol) and 4-pyridinecarboxaldehyde, 82.6 mg, 0.77 mmol. This compound was purified by means of a size exclusion chromatography in THF. Compound **4** was isolated as a yellow oil (296.8 mg, 65%). $C_{31}H_{64}N_4Si_3$ (576.44 g/mol). **^{1}H-NMR ($CDCl_3$):** δ −0.10 (s, 3H, -CH_2Si(CH_3)CH_2); −0.07 (s, 12H, -CH_2Si(CH_3)$_2$$CH_2$); 0.47 (m overlapping of signals, 14H, -CH_2Si(CH_3)CH_2 and -CH_2Si(CH_3)$_2$CH_2); 1.34 (m overlapping of signals, 10H, -NCH_2CH_2C$H_2$$CH_2$Si, -$SiCH_2CH_2$$CH_2$Si and -$(CH_3)_2SiCH_2CH_2$$CH_2$N); 1.70 (m, 2H, -$NCH_2CH_2$$CH_2CH_2$Si); 2.21 (m overlapping of signals, 16H, -CH_2N(CH_3)$_2$); 3.63 (t, ^3J $_{(H\text{-}H)}$ = 6.9 Hz, 2H, -NC$H_2$$CH_2CH_2CH_2$Si); 7.55 (m, 2H, Ar); 8.66 (m, 2H, Ar); 8.23 (s, 1H, -CH_{imine}). **^{13}C {^{1}H}-NMR ($CDCl_3$):** δ −4.9 (-CH_2Si(CH_3)CH_2); −3.2 (-CH_2Si(CH_3)$_2$$CH_2$); 13.0 (-$CH_2$Si($CH_3$)$_2$$CH_2$); 13.9 (-C$H_2$Si($CH_3$)$CH_2$); 18.5, 18.8, 20.1 (-Si$CH_2CH_2CH_2$Si); 21.8 (-$NCH_2CH_2CH_2$$CH_2$Si); 22.2 (-$(CH_3)_2SiCH_2CH_2CH_2$N); 34.7 (-$NCH_2CH_2CH_2CH_2$Si); 45.6 (-$CH_2$N(C$H_3$)$_2$); 61.6 (-N$CH_2CH_2CH_2CH_2$Si); 63.5 (-C$H_2$N($CH_3$)$_2$); 122.0, 143.2, 150.5 ($C_{Ar}$); 158.8 (-$CH_{imine}$). **^{29}Si-NMR ($CDCl_3$):** δ 1.1 (-$CH_2Si$($CH_3$)$CH_2$); 2.0 (-$CH_2Si$($CH_3$)$_2$$CH_2$). **^{15}N-NMR ($CDCl_3$):** δ −64.1 (-$N_{pyr}$); −32.2 (-$N_{imine}$); −352 (-N($CH_3$)$_2$). **Elemental analysis (%):** Calc.: C, 64.52; H, 11.18; N, 9.71; Exp.: C, 64.99; H, 10.79; N, 9.26. **MS:** $[M]^+ = 577.44$ uma.

4.2.5. Synthesis of [NCPh(p-N)]-G_2-[$(CH_2)_3N(CH_3)_2]_4$ (5)

The second generation dendron (**5**) was prepared and purified following the same procedure as for compound **4**, using the following reagents: NH_2-G_2-$[(CH_2)_3N(CH_3)_2]_4$ (352.7 mg, 0.27 mmol) and 4-pyridinecarboxaldehyde, (34.4 mg, 0.32 mmol) Compound **5** was isolated as a yellow oil (196.7 mg, 51%). $C_{59}H_{130}N_6Si_7$ (1120.33 g/mol).

^{1}H-NMR ($CDCl_3$): δ −0.10 (s, 9H, CH_2Si(CH_3)CH_2); −0.05 (s, 24H, -CH_2Si(CH_3)$_2$$CH_2$); 0.50 (m, overlapping of signals, 34H, -CH_2Si(CH_3)CH_2 and -CH_2Si(CH_3)$_2$CH_2); 1.38 (m, overlapping of signals, 22H, -NCH_2CH_2C$H_2$$CH_2$Si, -$SiCH_2CH_2$$CH_2$Si and -$(CH_3)_2SiCH_2CH_2$$CH_2$N); 1.72 (m, 2H, NCH_2C$H_2$$CH_2CH_2$Si); 2.20 (m, overlapping of signals, 32H, -CH_2N(CH_3)$_2$); 3.65 (t, 3J (H-H) = 6.9 Hz, 2H, -NC$H_2$$CH_2CH_2CH_2$Si); 7.57 (m, 2H, Ar); 8.67 (m, 2H, Ar); 8.25 (s, 1H, -CHimine). **^{13}C{^{1}H}-NMR ($CDCl_3$):** δ −4.9 (-CH_2Si(CH_3)CH_2); −3.2 (CH_2Si(CH_3)2CH_2); 13.0 (-CH_2Si(CH_3)$_2$$CH_2$); 13.9 (-C$H_2$Si($CH_3$)$CH_2$); 18.5, 18.7, 18.9, 19.0, 20.1 (-Si$CH_2CH_2CH_2$Si); 21.8 (-NCH_2CH_2C$H_2$$CH_2$Si); 22.1 ($(CH_3)_2SiCH_2CH_2CH_2$N); 34.7 (-$NCH_2CH_2CH_2CH_2$Si); 45.5 (-$CH_2$N(C$H_3$)$_2$); 61.7 (N$CH_2CH_2CH_2CH_2$Si); 63.5 (-C$H_2$N($CH_3$)$_2$); 121.9, 143.1, 150.4 (CAr); 158.7 (-CHimine). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-CH_2Si(CH_3)CH_2); 1.9 (-CH_2Si(CH_3)$_2$$CH_2$). **^{15}N-NMR ($CDCl_3$):** δ −64.2 (-$N_{pyr}$); −32.1 (-$N_{imine}$); −352 (-N($CH_3$)$_2$). **Elemental analysis (%):** Calc.: C, 63.25; H, 11.70; N, 7.50; Exp.: C, 63.79; H, 10.99; N, 7.73.

4.2.6. Synthesis of [NCPh(p-N)]-G_3-[$(CH_2)_3N(CH_3)_2]_8$ (6)

The third generation dendron (**6**) was prepared and purified following the same procedure as for compound **4**, using the following reagents: NH_2-G_3-$[(CH_2)_3N(CH_3)_2]_8$ (390.0 mg, 0.18 mmol de **IV**) and 4-pyridinecarboxaldehyde, 17.5 mg, 0.16 mmol. Compound **6** was isolated as a yellow oil (233.8 mg, 59%). $C_{115}H_{262}N_{10}Si_{15}$ (2260.71 g/mol).

^{1}H-NMR ($CDCl_3$): δ −0.10 (s, 21H, -CH_2Si(CH_3)CH_2); −0.05 (s, 48H, -CH_2Si(CH_3)$_2$$CH_2$); 0.48 (m, overlapping of signals, 74H, -CH_2Si(CH_3)CH_2 and -CH_2Si(CH_3)$_2$CH_2); 1.34 (m, overlapping of signals, 46H, -NCH_2CH_2C$H_2$$CH_2$Si, -$SiCH_2CH_2$$CH_2$Si and -$(CH_3)_2SiCH_2CH_2$$CH_2$N); 1.81 (m, 2H, NCH_2C$H_2$$CH_2CH_2$Si); 2.19 (m, overlapping of signals, 64H, -CH_2N(CH_3)$_2$); 3.67 (t, 3J (H-H) = 6.9 Hz, 2H, -NC$H_2$$CH_2CH_2CH_2$Si); 7.57 (m, 2H, Ar); 8.67 (m, 2H, Ar); 8.25 (s, 1H, -CHimine). **^{13}C{^{1}H}-NMR ($CDCl_3$):** δ −4.7 (-CH_2Si(CH_3)CH_2); −3.2 (CH_2Si(CH_3)$_2$$CH_2$); 13.0 (-$CH_2$Si($CH_3$)$_2$$CH_2$); 13.9 (-C$H_2$Si($CH_3$)$CH_2$); 18.5, 18.6, 18.9, 19.1 (-Si$CH_2CH_2CH_2$Si); 21.7 (-$NCH_2CH_2CH_2CH_2$Si); 22.2 (-$(CH_3)_2SiCH_2CH_2CH_2$N); 34.6 ($NCH_2CH_2CH_2CH_2$Si); 45.4 (-CH_2N(CH_3)$_2$); 61.7 (-N$CH_2CH_2CH_2CH_2$Si); 63.5 (CH_2N(CH_3)$_2$); 121.8, 143.2, 150.4 (CAr); 158.6 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.1 (CH_2Si(CH_3)CH_2); 1.9 (-CH_2Si(CH_3)$_2$$CH_2$). **^{15}N-NMR ($CDCl_3$):** δ −64.1 (-$N_{pyr}$); −32.2 ($N_{imine}$); −352 (-N($CH_3$)$_2$). **Elemental analysis** (%): Calc.: C, 62.59; H, 11.97; N, 6.35; Exp.: C, 63.19; H, 11.54; N, 6.73.

4.2.7. Synthesis of [NCPh(o-N)]-G_1-[$(CH_2)_3N(CH_3)_2]_2$ (7)

The compound (**7**) was prepared following the same procedure as for compound **1**, using the following reagents: NH_2-G_1-$[(CH_2)_3N(CH_3)_2]_2$ (341.7 mg, 0.69 mmol) and 2-pyridinecarboxaldehyde (73.0 mg, 0.67 mmol). This compound was purified by means of a size exclusion chromatography in THF. Compound **5** was isolated as brown-orange oil (209.0 mg, 52%).**^{1}H-NMR ($CDCl_3$):** δ −0.10 (s, 3H, -CH_2Si(CH_3)CH_2); −0.07 (s, 12H, -CH_2Si(CH_3)$_2$$CH_2$); 0.46 (m overlapping of signals, 14H, -CH_2Si(CH_3)CH_2 and -CH_2Si(CH_3)$_2$CH_2); 1.36 (m overlapping of signals, 10H, -NCH_2CH_2C$H_2$$CH_2$Si, -$SiCH_2CH_2$$CH_2$Si and -$(CH_3)_2SiCH_2CH_2$$CH_2$N); 1.72 (m, 2H, -$NCH_2CH_2$$CH_2CH_2$Si); 2.19 (m overlapping of signals, 16H, -CH_2N(CH_3)$_2$); 3.65 (t, ^3J $_{(H\text{-}H)}$ = 6.9 Hz, 2H, -NC$H_2$$CH_2CH_2CH_2$Si); 7.28 (m, 1H, Ar); 7.72 (m, 1H, Ar); 7.97 (m, 1H, Ar); 8.62 (m, 1H, Ar); 8.35 (s, 1H, -CH_{imine}). **^{13}C {^{1}H}-NMR ($CDCl_3$):** δ −4.9 (-CH_2Si(CH_3)CH_2); −3.2 (-CH_2Si(CH_3)$_2$$CH_2$); 13.0 (-$CH_2$Si($CH_3$)$_2$$CH_2$); 13.9 (-C$H_2$Si($CH_3$)$CH_2$); 18.5, 18.8, 20.2 (-Si$CH_2CH_2CH_2$Si); 21.9 (-$NCH_2CH_2CH_2CH_2$Si); 22.3 (-$(CH_3)_2SiCH_2CH_2CH_2$N); 34.8 (-$NCH_2CH_2CH_2CH_2$Si); 45.6 (-$CH_2$N(C$H_3$)$_2$); 61.5 (-N$CH_2CH_2CH_2CH_2$Si); 63.6 (-C$H_2$N($CH_3$)$_2$); 121.3, 124.7, 136.6, 149.5, 154.8 (C_{Ar}); 161.8 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.1 (-CH_2Si(CH_3)CH_2); 2.0 (-CH_2Si(CH_3)$_2$$CH_2$). **^{15}N-NMR ($CDCl_3$):** δ −67.2 (-$N_{pyr}$); −38.0 (-$N_{imine}$); −352 (-N($CH_3$)$_2$). **Elemental Analysis (%):** Calc. para $C_{31}H_{64}N_4Si_3$ (576.44 g/mol): C, 64.52; H, 11.18; N, 9.71; Exp.: C, 63.76; H, 10.87; N, 9.28. **MS:** $[M+H]^+ = 577.44$ uma.

4.2.8. Synthesis of [NCPh(o-N)]-G_2-[$(CH_2)_3N(CH_3)_2]_4$ (8)

The compound (**8**) was prepared following the same procedure as for compound **1**, using the following reagents: NH_2-G_2-$[(CH_2)_3N(CH_3)_2]_4$ (318.5 mg, 0.24 mmol) and 2-pyridinecarboxaldehyde (31.0 mg, 0.22 mmol). This compound was purified by means of a size exclusion column in THF.

Compound **6** was isolated as a brown orange oil (163.2 mg, 47%). **^{1}H-NMR ($CDCl_3$):** δ −0.13 (s, 9H, -$CH_2Si(CH_3)CH_2$); −0.08 (s, 24H, -$CH_2Si(CH_3)_2CH_2$); 0.45 (m overlapping of signals, 34H, -$CH_2Si(CH_3)CH_2$ and -$CH_2Si(CH_3)_2CH_2$); 1.33 (m overlapping of signals, 22H, -$NCH_2CH_2CH_2CH_2Si$, -$SiCH_2CH_2CH_2Si$ and -$(CH_3)_2SiCH_2CH_2CH_2N$); 1.69 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 2.17 (m overlapping of signals, 32H, -$CH_2N(CH_3)_2$); 3.62 (t, ^3J $_{(H-H)}$ = 6.9 Hz, 2H, -$NCH_2CH_2CH_2CH_2Si$); 7.25 (m, 1H, Ar); 7.66 (m, 1H, Ar); 7.92 (m, 1H, Ar); 8.56 (m, 1H, Ar); 8.31 (s, 1H, -CH_{imine}). **^{13}C{^{1}H}-NMR ($CDCl_3$):** δ −4.8 (-$CH_2Si(CH_3)CH_2$); −3.2 (-$CH_2Si(CH_3)_2CH_2$); 13.0 (-$CH_2Si(CH_3)_2CH_2$); 13.9 (-$CH_2Si(CH_3)CH_2$); 18.6, 18.9, 19.1, 20.2 (-$SiCH_2CH_2CH_2Si$); 21.9 (-$NCH_2CH_2CH_2CH_2Si$); 22.2 (-$(CH_3)_2SiCH_2CH_2CH_2N$); 34.9 (-$NCH_2CH_2CH_2CH_2Si$); 45.6 (-$CH_2N(CH_3)_2$); 61.5 (-$NCH_2CH_2CH_2CH_2Si$); 63.6 (-$CH_2N(CH_3)_2$); 121.3, 124.7, 136.6, 149.5, 154.8 (C_{Ar}); 161.7 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-$CH_2Si(CH_3)CH_2$); 1.9 (-$CH_2Si(CH_3)_2CH_2$). **^{15}N-NMR ($CDCl_3$):** δ −67.1 (-N_{pyr}); −37.9 (-N_{imine}); −352 (-$N(CH_3)_2$). **Elemental analysis (%):** Calc. $C_{59}H_{130}N_6Si_7$ (1120.33 g/mol): C, 63.25; H, 11.70; N, 7.50; Exp.: C, 62.69; H, 11.15; N, 6.93.

4.2.9. Synthesis of [NCPh(o-N)]-G$_3$-[(CH$_2$)$_3$N(CH$_3$)$_2$]$_8$ (9)

Compound (**9**) was prepared following the same procedure as for compound **1**, using the following reagents: NH_2-G_3-$[(CH_2)_3N(CH_3)_2]_8$ (376.3 mg, 0.17 mmol) and 2-pyridinecarboxaldehyde (16.8 mg, 0.15 mmol). This compound was purified by means of a size exclusion column in THF. Compound **9** was isolated as a brown orange oil (196.4 mg, 49%). $C_{115}H_{262}N_{10}Si_{15}$ (2260.71 g/mol). **^{1}H-NMR (CDCl3):** δ −0.08 (s, 21H, -$CH_2Si(CH_3)CH_2$); −0.04 (s, 48H, -$CH_2Si(CH_3)_2CH_2$); 0.53 (m, overlapping of signals, 74H, -$CH_2Si(CH_3)CH_2$ and -$CH_2Si(CH_3)_2CH_2$); 1.31 (m, overlapping of signals, 46H, -$NCH_2CH_2CH_2CH_2Si$, -$SiCH_2CH_2CH_2Si$ and -$(CH_3)_2SiCH_2CH_2CH_2N$); 1.74 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 2.22 (m, overlapping of signals, 64H, $CH_2N(CH_3)_2$); 3.68 (t, 3J (H-H) = 6.9 Hz, 2H, -$NCH_2CH_2CH_2CH_2Si$); 7.31 (m, 1H, Ar); 7.72 (m, 1H, Ar); 7.95 (m, 1H, Ar); 8.62 (m, 1H, Ar); 8.35 (s, 1H, -CH_{imine}). **^{13}C{^{1}H}-NMR ($CDCl_3$):** δ −4.8 (-$CH_2Si(CH_3)CH_2$); −3.1 (-$CH_2Si(CH_3)_2CH_2$); 13.0 (-$CH_2Si(CH_3)_2CH_2$); 13.8 (-$CH_2Si(CH_3)CH_2$); 18.6, 18.7, 18.9, 19.1 (-$SiCH_2CH_2CH_2Si$); 21.9 ($NCH_2CH_2CH_2CH_2Si$); 22.1 (-$(CH_3)_2SiCH_2CH_2CH_2N$); 34.8 (-$NCH_2CH_2CH_2CH_2Si$); 45.4 (-$CH_2N(CH_3)_2$); 61.6 (-$NCH_2CH_2CH_2CH_2Si$); 63.4 (-$CH_2N(CH_3)_2$); 121.1, 124.5, 136.4, 149.2, 154.6 (CAr); 161.4 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.1 (-$CH_2Si(CH_3)CH_2$); 1.9 ($CH_2Si(CH_3)_2CH_2$). **^{15}N-NMR ($CDCl_3$):** δ −67.3 (-N_{pyr}); −38.1 (-N_{imine}); −352 (-$N(CH_3)_2$). **Elemental analysis (%):** Calc. C, 62.59; H, 11.97; N, 6.35; Exp.: C, 63.07; H, 11.48; N, 6.82.

4.2.10. Synthesis of [NCPh(o-O)]-G$_1$-[(CH$_2$)$_3$N(CH$_3$)$_2$]$_2$ (10)

Compound **10** was prepared as compound **3** and purified following the same procedure as for compound **4**, using the following reagents: NH_2-G_1-$[(CH_2)_3N(CH_3)_2]_2$ (313.2 mg, 0.64 mmol and salicylaldehyde (75.9 mg, 0.62 mmol). Compound **10** was isolated as a yellow oil (236.4 mg, 62%). $C_{32}H_{65}N_3OSi_3$ (591.44 g/mol).**^{1}H-NMR ($CDCl_3$):** δ −0.09 (s, 3H, $CH_2Si(CH_3)CH_2$); −0.06 (s, 12H, -$CH_2Si(CH_3)_2CH_2$); 0.47 (m, overlapping of signals, 14H, -$CH_2Si(CH_3)CH_2$ and -$CH_2Si(CH_3)_2CH_2$); 1.34 (m, overlapping of signals, 10H, -$NCH_2CH_2CH_2CH_2Si$, -$SiCH_2CH_2CH_2Si$ and -$(CH_3)_2SiCH_2CH_2CH_2N$); 1.69 (m, 2H, $NCH_2CH_2CH_2CH_2Si$); 2.20 (m, overlapping of signals, 16H, -$CH_2N(CH_3)_2$); 3.57 (t, 3J (H-H) = 6.9 Hz, 2H, -$NCH_2CH_2CH_2CH_2Si$); 6.85 (m, 1H, Ar); 6.93 (m, 1H, Ar); 7.26 (m, 2H, Ar); 8.32 (s, 1H, -CH_{imine}); 13.62 (s, 1H, -O*H*). **^{13}C{^{1}H}-NMR ($CDCl_3$):** δ −4.9 (-$CH_2Si(CH_3)CH_2$); −3.2 (-$CH_2Si(CH_3)_2CH_2$); 13.0 (-$CH_2Si(CH_3)_2CH_2$); 13.8 ($CH_2Si(CH_3)CH_2$); 18.5, 18.8, 20.2 (-$SiCH_2CH_2CH_2Si$); 21.7 (-$NCH_2CH_2CH_2CH_2Si$); 22.2 (-$(CH_3)_2SiCH_2CH_2CH_2N$); 34.9 (-$NCH_2CH_2CH_2CH_2Si$); 45.6 (-$CH_2N(CH_3)_2$); 59.4 ($NCH_2CH_2CH_2CH_2Si$); 63.6 (-$CH_2N(CH_3)_2$); 117.1, 118.5, 118.9, 131.1, 132.1, 161.5 (CAr); 164.5 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-$CH_2Si(CH_3)CH_2$); 2.0 (-$CH_2Si(CH_3)_2CH_2$). **^{15}N NMR ($CDCl_3$):** δ −81.9 (-N_{imine}); −352 (-$N(CH_3)_2$). **Elemental analysis (%):** Calc.: C, 64.91; H, 11.06; N, 7.10; Exp.: C, 64.45; H, 10.63; N, 6.84. MS: $[M+H]^+ = 592.44$ uma.

4.2.11. Synthesis of [NCPh(o-O)]-G$_2$-[(CH$_2$)$_3$N(CH$_3$)$_2$]$_4$ (11)

Compound **11** was prepared as compound **3** and purified following the same procedure as for compound **4**, using the following reagents: NH_2-G_2-$[(CH_2)_3N(CH_3)_2]_4$ (250.5 mg, 0.24 mmol) and salicylaldehyde (27.1 mg, 0.22 mmol). Compound **11** was isolated as a yellow oil (173.2 mg, 63%). $C_{60}H_{131}N_5OSi_7$ (1135.34 g/mol). **^{1}H-NMR ($CDCl_3$):** δ −0.09 (s, 9H, $CH_2Si(CH_3)CH_2$); −0.06 (s, 24H, -$CH_2Si(CH_3)_2CH_2$); 0.47 (m, overlapping of signals, 34H, -$CH_2Si(CH_3)CH_2$ and -$CH_2Si(CH_3)_2CH_2$); 1.34 (m, overlapping of signals, 22H, -$NCH_2CH_2CH_2CH_2Si$, -$SiCH_2CH_2CH_2Si$ and -$(CH_3)_2SiCH_2CH_2CH_2N$); 1.69 (m, 2H, $NCH_2CH_2CH_2CH_2Si$); 2.20 (m, overlapping of signals, 32H, -$CH_2N(CH_3)_2$); 3.57 (t, 3J (H-H) = 6.9 Hz, 2H, -$NCH_2CH_2CH_2CH_2Si$); 6.85 (m, 1H, Ar); 6.93 (m, 1H, Ar); 7.26 (m, 2H, Ar); 8.32 (s, 1H, -CH_{imine}); 13.62 (s, 1H, -O*H*). **^{13}C{^{1}H}-NMR ($CDCl_3$):** δ −4.9 (-$CH_2Si(CH_3)CH_2$); −3.2 (-$CH_2Si(CH_3)_2CH_2$); 13.0 (-$CH_2Si(CH_3)_2CH_2$); 13.8 ($CH_2Si(CH_3)CH_2$); 18.5, 18.8,19.1, 20.2 (-$SiCH_2CH_2CH_2Si$); 21.7 (-$NCH_2CH_2CH_2CH_2Si$); 22.2 (-$(CH_3)_2SiCH_2CH_2CH_2N$); 34.9 (-$NCH_2CH_2CH_2CH_2Si$); 45.6 (-$CH_2N(CH_3)_2$); 59.3 ($NCH_2CH_2CH_2CH_2Si$); 63.6 (-$CH_2N(CH_3)_2$); 117.1, 118.5, 118.9, 131.1, 132.1, 161.5 (CAr); 164.5 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-$CH_2Si(CH_3)CH_2$); 1.9 (-$CH_2Si(CH_3)_2CH_2$). **^{15}N-NMR ($CDCl_3$):** δ −82.0 (-N_{imine}); −352 (-$N(CH_3)_2$). **Elemental analysis (%):** Calc.: C, 63.48; H, 11.63; N, 6.17; Exp.: C, 64.15; H, 11.24; N, 6.59.

4.2.12. Synthesis of [NCPh(o-O)]-G$_3$-[(CH$_2$)$_3$N(CH$_3$)$_2$]$_8$ (12)

Compound **12** was prepared and purified following the same procedure as for compound **3**, using the following reagents: NH_2-G_3-$[(CH_2)_3N(CH_3)_2]_8$ (206.8 mg, 0.09 mmol) and salicylaldehyde (9.4 mg, 0.07 mmol). $C_{116}H_{263}N_9OSi_{15}$ (2221.72 g/mol). Compound **12** was isolated as a yellow oil (128.3 mg, 59%). **^{1}H-NMR ($CDCl_3$):** δ −0.08 (s, 21H, $CH_2Si(CH_3)CH_2$); −0.04 (s, 48H, -$CH_2Si(CH_3)_2CH_2$); 0.53 (m, overlapping of signals, 74H, -$CH_2Si(CH_3)CH_2$ and -$CH_2Si(CH_3)_2CH_2$); 1.31 (m, overlapping of signals, 46H, -$NCH_2CH_2CH_2CH_2Si$, -$SiCH_2CH_2CH_2Si$ and -$(CH_3)_2SiCH_2CH_2CH_2N$); 1.69 (m, 2H, $NCH_2CH_2CH_2CH_2Si$); 2.20 (m, overlapping of signals, 64H, -$CH_2N(CH_3)_2$); 3.57 (t, 3J (H-H) = 6,9 Hz, 2H, -$NCH_2CH_2CH_2CH_2Si$); 6.85 (m, 1H, Ar); 6.93 (m, 1H, Ar); 7.26 (m, 2H, Ar); 8.32 (s, 1H, -CH_{imine}); 13.62 (s, 1H, -O*H*). **^{13}C{^{1}H}-NMR ($CDCl_3$):** δ 4.7 (-$CH_2Si(CH_3)CH_2$); −3.2 (-$CH_2Si(CH_3)_2CH_2$); 13.0 (-$CH_2Si(CH_3)_2CH_2$); 13.9 ($CH_2Si(CH_3)CH_2$); 18.6, 18.7, 18.9, 19.1 (-$SiCH_2CH_2CH_2Si$); 21.9 (-$NCH_2CH_2CH_2CH_2Si$); 22.1 (-$(CH_3)_2SiCH_2CH_2CH_2N$); 34.8 (-$NCH_2CH_2CH_2CH_2Si$); 45.4 (-$CH_2N(CH_3)_2$); 59.2 ($NCH_2CH_2CH_2CH_2Si$); 63.4 (-$CH_2N(CH_3)_2$); 117.2, 118.5, 118.9, 131.2, 132.1, 161.4 (CAr); 164.6 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-$CH_2Si(CH_3)CH_2$); 1.9 (-$CH_2Si(CH_3)_2CH_2$). **^{15}N-NMR ($CDCl_3$):** δ −83.0 (-N_{imine}); −352 (-$N(CH_3)_2$). **Elemental analysis (%):** Calc. C, 62.71; H, 11.93; N, 5.67; Exp.: C, 63.47; H, 11.29; N, 5.01.

4.2.13. Synthesis of [Cl$_2$(η^6-p-cymene)RuNH$_2$]-G$_1$-A$_2$ (13)

To a solution containing the dendritic ligand NH_2-G_1-A_2 (49.2 mg, 0.24 mmol), in dichloromethane, the dimer $[Ru(\eta^6\text{-p-cymene})Cl_2]_2$ was added slowly (76.2 mg, 0.24 mmol). The reaction was kept under constant stirring at room temperature for 2 h and then the solvent is removed to dryness. Compound **13** was isolated as an orange oil (98.7 mg, 78%). $C_{21}H_{37}Cl_2NRuSi$ (503.59 g/mol). **^{1}H-NMR ($CDCl_3$):** δ −0.01 (s, 3H, -$CH_2Si(CH_3)(CH_2)_2$); 0.55 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 1.35 (m, overlapping of signals, 8H,

-$NCH_2CH_2CH_2CH_2Si$ and -$(CH_3)_2CH_{cym}$); 1.56 (m, overlapping of signals, 6H, -$CH_2Si(CH_3)(CH_2)_2$) and -$NCH_2CH_2CH_2CH_2Si$); 2.26 (s, 3H, -CH_{3cym}); 2.75 (m, 2H, -NH_2); 3.02 (m, overlapping of signals, 3H, -$(CH_3)_2CH_{cym}$ and -$NCH_2CH_2CH_2CH_2Si$); 4.87 (m, 4H, -$Si(CH_2CHCH_2)_2$); 5.26 (m, 2H, Ar_{cym}); 5.40 (m, 2H, Ar_{cym}); 5.75 (m, 2H, -$Si(CH_2CHCH_2)_2$). **^{13}C {^{1}H}-NMR($CDCl_3$):** δ −5.7 (-$CH_2Si(CH_3)(CH_2)_2$); 12.9 (-$NCH_2CH_2CH_2CH_2Si$); 19.0 (-CH_{3cym}); 20.9 (-$NCH_2CH_2CH_2CH_2Si$); 21.3 (-$CH_2Si(CH_3)(CH_2)_2$); 22.3 (-$(CH_3)_2CH_{cym}$); 31.0 (-$(CH_3)_2CH_{cym}$); 37.2 (-$NCH_2CH_2CH_2CH_2Si$); 49.3 (-$NCH_2CH_2CH_2CH_2Si$); 80.6, 80.7 (-CH_{cym}); 96.2, 102.4 (C_{cym}); 113.4 (-$Si(CH_2CHCH_2)_2$); 134.6 (-$Si(CH_2CHCH_2)_2$). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-$CH_2Si(CH_3)(CH_2)_2$). **Elemental analysis (%):** Calc.: C, 50.09; H, 7.41; N, 2.78; Exp.: C, 50.51; H, 7.03; N, 3.18.

4.2.14. Synthesis of [$Cl_2(\eta^6$-p-cymene)RuNCPh(p-N)]-G_1-A_2 (14)

Compound **14** was prepared following the same procedure as for compound **13**, using the following reagents: [NCPh(*p*-N)]-G_1-A_2 (43,4 mg, 0,15 mmol of **1**) and [Ru(η^6-*p*-cimeno)Cl_2]$_2$ (46.4 mg, 0.15 mmol). Compound **14** was isolated as an orange oil (78.3 mg, 85%). $C_{27}H_{40}Cl_2N_2RuSi$ (592.69 g/mol). **^{1}H-NMR ($CDCl_3$):** δ −0.02 (s, 3H, -$CH_2Si(CH_3)(CH_2)_2$); 0.60 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 1.30 (m, 6H, -$(CH_3)_2CH_{cym}$); 1.39 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 1.55 (m, 4H, -$CH_2Si(CH_3)(CH_2)_2$); 1.72 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 2.09 (s, 3H, -CH_{3cym}); 2.98 (m, 1H, -$(CH_3)_2CH_{cym}$); 3.68 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 4.84 (m, 4H, -$Si(CH_2CHCH_2)_2$); 5.22 (m, 2H, Ar_{cym}); 5.44 (m, 2H, Ar_{cym}); 5.75 (m, 2H, -$Si(CH_2CHCH_2)_2$); 7.58 (m, 2H, Ar); 9.08 (m, 2H, Ar); 8.26 (s, 1H, -CH_{imine}). **^{13}C {^{1}H}-NMR ($CDCl_3$):** δ −5.7 (-$CH_2Si(CH_3)(CH_2)_2$); 12.9 (-$NCH_2CH_2CH_2CH_2Si$); 18,4 (-CH_{3cym}); 20.9 (-$NCH_2CH_2CH_2CH_2Si$); 21.3 (-$CH_2Si(CH_3)(CH_2)_2$); 22.3 (-$(CH_3)_2CH_{cym}$); 31.0 (-$(CH_3)_2CH_{cym}$); 34.4 (-$NCH_2CH_2CH_2CH_2Si$); 61.7 (-$NCH_2CH_2CH_2CH_2Si$); 82.3, 83.2 (-CH_{cym}); 97.4, 103.7 (C_{cym}); 113.3 (-$Si(CH_2CHCH_2)_2$); 134.8 (-$Si(CH_2CHCH_2)_2$); 122.5, 144.6, 155.4 (C_{Ar}); 159.0 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-$CH_2Si(CH_3)(CH_2)_2$). **Elemental Analysis (%):** Calc. C, 54.72; H, 6.80; N, 4.73; Exp.: C, 54.12; H, 6.58; N, 4.38.

4.2.15. Synthesis of [[Cl(η^6-p-cymene)RuNCPh(o-N)]-G_1-A_2]Cl (15)

Compound **15** was prepared following the same procedure as for compound **13**, using the following reagents: [NCPh(*o*-N)]-G_1-A_2 (47.1 mg, 0.16 mmol) and [Ru(η^6-*p*-cimeno)Cl_2]$_2$ (50.3 mg, 0.16 mmol). Compound **15** was isolated as an orange oil (55.5 mg, 57%). $C_{27}H_{40}Cl_2N_2RuSi$ (592.69 g/mol). **^{1}H-NMR ($CDCl_3$):** δ −0.02 (s, 3H, -$CH_2Si(CH_3)(CH_2)_2$); 0.61 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 1.06 (m, 3H, -$(CH_3)_2CH_{cym}$); 1.07 (m, 3H, -$(CH_3)_2CH_{cym}$); 1.42 (m, 2H, -$NCH_2CH_2CH_2CH_2Si(CH_3)$); 1.54 (m, 4H, -$CH_2Si(CH_3)(CH_2)_2$); 2.00 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 2.25 (s, 3H, -$CH_{3cym}$); 2.76 (m, 1H, -$(CH_3)_2CH_{cym}$); 4.43 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 4.84 (m, 4H, -$Si(CH_2CHCH_2)_2$); 5.76 (m, overlapping of signals, 3H, -$Si(CH_2CHCH_2)_2$ and Ar_{cym}); 5.93 (m, 1H, Ar_{cym}); 6.00 (m, 1H, Ar_{cym}); 6.21 (m, 1H, Ar_{cym}); 7.68 (m, 1H, Ar); 7.98 (m, 1H, Ar); 8.30 (m, 1H, Ar); 9.81 (m, 1H, Ar); 8.99 (s, 1H, -CH_{imine}). **^{13}C {^{1}H}-NMR ($CDCl_3$):** δ −5.7 (-$CH_2Si(CH_3)(CH_2)_2$); 12.9 (-$NCH_2CH_2CH_2CH_2Si$); 18.8 (-CH_{3cym}); 21.2 (-$NCH_2CH_2CH_2CH_2Si$ and -$CH_2Si(CH_3)(CH_2)_2$); 21.9, 22.4 (-$(CH_3)_2CH_{cym}$); 31.1 (-$(CH_3)_2CH_{cym}$); 33.5 (-$NCH_2CH_2CH_2CH_2Si$); 67.0 (-$NCH_2CH_2CH_2CH_2Si$); 84.6, 85.4, 85.7, 87.1 (-CH_{cym}); 102.3, 106.2 (C_{cym}); 113.2 (-$Si(CH_2CHCH_2)_2$); 134.6 (-$Si(CH_2CHCH_2)_2$); 128.9, 129.2, 139.4, 154.4, 156.7 (C_{Ar}); 167.0 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-$CH_2Si(CH_3)(CH_2)_2$). **Elemental Analysis (%):** Calc. C, 54.72; H, 6.80; N, 4.73; Exp.: C, 54.27; H, 6.59; N, 4.71.. **MS:** $[M]^+ = 557.17$ uma.

4.2.16. Synthesis of [Cl(η^6-p-cimeno)RuNCPh(o-O)]-G_1-A_2 (16)

To a solution of dendron **3** [NCPh(*o*-OH)]-G_1-A_2 (38.6 mg, 0.13 mmol) in ethanol, trimethylamine (12.95 mg, 0.13 mmol) was added. The yellow solution was kept under constant stirring for 30 min at room temperature. Immediately, the dimer [Ru(η^6-p-cymene)Cl_2]$_2$ (39.2 mg, 0.06 mmol) was added to the reaction mixture and allowed to react for 5 h at room temperature. The solvent was removed in vacuo and the resulting oil was purified by extraction of CH_2Cl_2/H_2O to remove the ammonium salt formed during the reaction. Then, the organic phase is dried $MgSO_4$ and the solution is filtered and the solvent is evaporated. Compound **16** was isolated as a brown oil (18.7 mg, 51%). $C_{28}H_{40}ClNORuSi$ (571.24 g/mol). **^{1}H-NMR ($CDCl_3$):** δ −0.02 (s, 3H, -$CH_2Si(CH_3)(CH_2)_2$); 0.65 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 1.11 (m, 3H, -$(CH_3)_2CH_{cym}$); 1.23 (m, 3H, -$(CH_3)_2CH_{cym}$); 1.42 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 1.59 (m, 4H, -$CH_2Si(CH_3)(CH_2)_2$); 1.92 (m, 1H, -$NCH_2CH_2CH_2CH_2Si$); 2.07 (m, 1H, -$NCH_2CH_2CH_2CH_2Si$); 2.20 (s, 3H, -CH_{3cym}); 2.77 (m, 1H, -$(CH_3)_2CH_{cym}$); 4.04 (m, 1H, -$NCH_2CH_2CH_2CH_2Si$); 4.17 (m, 1H, -$NCH_2CH_2CH_2CH_2Si$); 4.84 (m, 4H, -$Si(CH_2CHCH_2)_2$); 5.03 (m, 1H, Ar_{cym}); 5.39 (m, 3H, Ar_{cym}); 5.77 (m, 2H, -$Si(CH_2CHCH_2)_2$); 6.40 (m, 1H, Ar); 6.91 (m, 2H, Ar); 7.15 (m, 1H, Ar); 7.66 (s, 1H, -CH_{imine}). **^{13}C {^{1}H}-NMR ($CDCl_3$):** δ −5.7 (-$CH_2Si(CH_3)(CH_2)_2$); 13.2 (-$NCH_2CH_2CH_2CH_2Si$); 18.8 (-CH_{3cym}); 21.4 (-$NCH_2CH_2CH_2CH_2Si$); 21.8 (-$CH_2Si(CH_3)(CH_2)_2$); 22.9 (-$(CH_3)_2CH_{cym}$); 29.8 (-$(CH_3)_2CH_{cym}$); 31.1 (-$(CH_3)_2CH_{cym}$); 33.5 (-$NCH_2CH_2CH_2CH_2Si$); 69.0 (-$NCH_2CH_2CH_2CH_2Si$); 80.2, 82.1, 83.3, 85.8 (-CH_{cym}); 97.2, 101.7 (C_{cym}); 113.4 (-$Si(CH_2CHCH_2)_2$); 134.7 (-$Si(CH_2CHCH_2)_2$); 114.2, 119.5, 122.5, 134.4, 134.6, 163.5 (C_{Ar}); 165.1 (-CH_{imine}). **^{29}Si-NMR ($CDCl_3$):** δ 1.2 (-$CH_2Si(CH_3)(CH_2)_2$). **Elemental Analysis (%):** Calc. C, 58.87; H, 7.06; N, 2.45; Exp.: C, 58.65; H, 6.90; N, 2.67.

4.2.17. Synthesis of [$Cl_2(\eta^6$-p-cymene)RuNH$_2$]-G_1-[$(CH_2)_3N(CH_3)_2$]$_2$ (17)

Compound **17** was prepared following the same procedure as for compound **13**, using the following reagents: NH_2-G_1-[$(CH_2)_3N(CH_3)_2$]$_2$ (49.2 mg, 0.24 mmol) and [Ru(η^6-*p*-cimeno)Cl_2]$_2$ (76.2 mg, 0.24 mmol). Compound **17** was isolated as an orange oil (98.7 mg, 78%). $C_{35}H_{75}Cl_2N_3RuSi_3$ (794.23 g/mol). **^{1}H-NMR ($CDCl_3$):** δ −0.09 (s, 3H, -$CH_2Si(CH_3)CH_2$); −0.05 (s, 12H, -$CH_2Si(CH_3)_2CH_2$); 0.50 (m, overlapping of signals, 14H, -$CH_2Si(CH_3)CH_2$ and -$CH_2Si(CH_3)_2CH_2$); 1.29 (m, overlapping of signals, 16H, -$NCH_2CH_2CH_2CH_2Si$, -$SiCH_2CH_2CH_2Si$, -$(CH_3)_2SiCH_2CH_2CH_2N$ and -$(CH_3)_2CH_{cym}$); 1.46 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 2.26 (m, overlapping of signals, 19H, -$CH_2N(CH_3)_2$ and -CH_{3cym}); 2.79 (m, 2H, -NH_2); 3.00 (m overlapping of signals, 3H, -$(CH_3)_2CH_{cym}$ and -$NCH_2CH_2CH_2CH_2Si$); 5.28 (m, 2H, Ar_{cym}); 5.40 (m, 2H, Ar_{cym}). **^{13}C {^{1}H}-NMR ($CDCl_3$):** δ −5.0 (-$CH_2Si(CH_3)CH_2$); −3.2 (-$CH_2Si(CH_3)_2CH_2$); 12.9 (-$CH_2Si(CH_3)_2CH_2$); 14.0 (-$CH_2Si(CH_3)CH_2$); 18.5, 18.8, 20.1 (-$SiCH_2CH_2CH_2Si$); 18.9 (-CH_{3cym}); 21.3 (-$NCH_2CH_2CH_2CH_2Si$); 21.9 (-$(CH_3)_2SiCH_2CH_2CH_2N$); 22.4 (-$(CH_3)_2CH_{cym}$); 31.0 (-$(CH_3)_2CH_{cym}$); 37.6 (-$NCH_2CH_2CH_2CH_2Si$); 45.4 (-$CH_2N(CH_3)_2$); 49.5 (-$NCH_2CH_2CH_2CH_2Si$); 63.3 (-$CH_2N(CH_3)_2$); 80.5, 80.8 (-CH_{cym}); 96.2, 102.5 (C_{cym}). **^{29}Si-NMR ($CDCl_3$):** δ 1.1 (-$CH_2Si(CH_3)CH_2$); 2.0 (-$CH_2Si(CH_3)_2CH_2$). **Elemental analysis (%):** Calc. C, 52.93; H, 9.52; N, 5.29; Exp.: C, 52.96; H, 9.56; N, 5.62.

4.2.18. Synthesis of [$Cl_2(\eta^6$-p-cymene)RuNCPh(p-N)]-G_1-[$(CH_2)_3N(CH_3)_2$]$_2$ (18)

Compound **18** was prepared following the same procedure as for compound **13**, using the following reagents: [NCPh(*p*-N)]-G_1-[$(CH_2)_3N(CH_3)_2$]$_2$ (60.2 mg, 0.10 mmol) and [Ru(η^6-*p*-cimeno)Cl_2]$_2$ (31.9 mg, 0.10 mmol). Compound **18** was isolated as an orange oil (43.7 mg, 49%).$C_{41}H_{78}Cl_2N_4RuSi_3$ (883.33 g/mol). **^{1}H-NMR ($CDCl_3$):** δ −0.08 (s, 3H, -$CH_2Si(CH_3)CH_2$); −0.04 (s, 12H, -$CH_2Si(CH_3)_2CH_2$); 0.48 (m, overlapping of signals, 14H, -$CH_2Si(CH_3)CH_2$ and -$CH_2Si(CH_3)_2CH_2$); 1.45 (m, overlapping of signals, 16H, -$(CH_3)_2CH_{cym}$), -$NCH_2CH_2CH_2CH_2Si$, -$SiCH_2CH_2CH_2Si$ and -$(CH_3)_2SiCH_2CH_2CH_2N$); 1.72 (m, 2H, -$NCH_2CH_2CH_2CH_2Si$); 2.09 (s,

3H, -CH_{3cym}); 2.28 (m, overlapping of signals, 16H, -CH$_2$N(CH_3)$_2$ and -CH_2N(CH$_3$)$_2$); 2.65 (m, 1H, -(CH$_3$)$_2$CH_{cim}); 3.65 (m, 2H, -NCH_2CH$_2$CH$_2$CH$_2$Si); 5.21 (m, 2H, Ar$_{cym}$); 5.46 (m, 2H, Ar$_{cym}$); 7.59 (m, 2H, Ar); 9.05 (m, 2H, Ar); 8.26 (s, 1H, -CH_{imine}). **^{13}C {^{1}H}-NMR (CDCl$_3$):** δ −5.0 (-CH$_2$Si(CH_3)CH$_2$); −3.2 (-CH$_2$Si(CH_3)$_2$CH$_2$); 12.7 (-CH$_2$Si(CH$_3$)$_2$CH_2); 14.1 (-CH_2Si(CH$_3$)CH$_2$); 18.5, 18.6, 20.2 (-SiCH$_2$CH$_2$CH$_2$Si); 18.4 (-CH_{3cym}); 21.0 (-NCH$_2$CH$_2$CH_2CH$_2$Si); 21.8 (-(CH$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); 22.3 (-(CH_3)$_2$CH$_{cym}$); 31.1 (-(CH$_3$)$_2$CH_{cim}); 37.8 (-NCH$_2$CH$_2$CH$_2$CH$_2$Si); 45.4 (-CH$_2$N(CH_3)$_2$); 49.5 (-NCH$_2$CH$_2$CH$_2$CH$_2$Si); 63.1 (-CH$_2$N(CH$_3$)$_2$); 82.5, 83.1 (-CH$_{cym}$); 97.6, 103.5 (C$_{cym}$); 122.3, 144.6, 155.3 (C$_{Ar}$); 159.1 (-CH_{imine}). **^{29}Si-NMR (CDCl$_3$):** δ 1.1 (-CH$_2$Si(CH$_3$)CH$_2$); 2.0 (-CH$_2$Si(CH$_3$)$_2$CH$_2$). **Elemental Analysis (%):** Calc. C, 55.75; H, 8.90; N, 6.34; Exp.: C, 55.96; H, 9.38; N, 5.82.

4.2.19. Synthesis of [[Cl(η^6-p-cymene)RuNCPh(o-N)]-G$_1$-[(CH$_2$)$_3$N(CH$_3$)$_2$]$_2$]Cl (19)

Compound **19** was prepared following the same procedure as for compound **13**, using the following reagents in methanol: [NCPh(*o*-N)]-G$_1$-[(CH$_2$)$_3$N(CH$_3$)$_2$]$_2$ (53.1 mg, 0.09 mmol) and [Ru(η^6-*p*-cimeno)Cl$_2$]$_2$ (28.2 mg, 0.05 mmol). Compound **19** was isolated as a red solid (21.3 mg, 52%). **^{1}H-NMR (CD$_3$OD):** δ −0.06 (s, 3H, -CH$_2$Si(CH_3)CH$_2$); −0.03 (s, 12H, -CH$_2$Si(CH_3)$_2$CH$_2$); 0.54 (m overlapping of signals, 14H, CH_2Si(CH$_3$)CH_2 and -CH_2Si(CH$_3$)$_2$CH_2); 1.05 (d, $^3J_{(H\text{-}H)}$ = 6.9 Hz, 3H, -(CH_3)$_2$CH$_{cim}$); 1,15 (d, $^3J_{(H\text{-}H)}$ = 6.9 Hz, 3H, -(CH_3)$_2$CH$_{cim}$); 1.45 (m overlapping of signals, 10H, -NCH$_2$CH$_2$CH_2CH$_2$Si, -SiCH$_2$CH_2CH$_2$Si -(CH$_3$)$_2$SiCH$_2$CH_2CH$_2$N); 2.01 (m, 2H, -NCH$_2$CH_2CH$_2$CH$_2$Si); 2.28 (s, 3H, -CH_{3cim}); 2.30 (m, 12H, -CH$_2$N(CH_3)$_2$); 2.38 (m, 4H, -CH_2N(CH$_3$)$_2$); 2.68 (m, 1H, -(CH$_3$)$_2$CH_{cim}); 4.30 (m, 1H, -NCH_2CH$_2$CH$_2$CH$_2$Si); 4.60 (m, 1H, -NCH_2CH$_2$CH$_2$CH$_2$Si); 5.84 (m, 2H, Ar$_{cim}$); 6.09 (m, 1H, Ar$_{cim}$); 6.16 (m, 1H, Ar$_{cim}$); 7.81 (m, 1H, Ar); 8.15 (m, 1H, Ar); 8.24 (m, 1H, Ar); 9.49 (m, 1H, Ar); 8.69 (s, 1H, -CH_{imine}). **^{13}C {^{1}H}-NMR (CD$_3$OD):** δ −4.8 (-CH$_2$Si(CH_3)CH$_2$); −3.2 (-CH$_2$Si(CH_3)$_2$CH$_2$); 13.6 (-CH$_2$Si(CH$_3$)$_2$CH_2); 14.7 (-CH_2Si(CH$_3$)CH$_2$); 19.7, 19.9, 20.1 (-SiCH$_2$CH$_2$CH$_2$Si); 19.0 (-CH_{3cim}); 22.2 (-NCH$_2$CH$_2$CH_2CH$_2$Si); 22.5 (-SiCH$_2$CH$_2$CH$_2$N); 21.9, 22.8 (-(CH_3)$_2$CH$_{cim}$); 32.0 (-(CH$_3$)$_2$CH_{cim}); 34.7 (-NCH$_2$CH$_2$CH$_2$CH$_2$Si); 45.2 (-CH$_2$N(CH_3)$_2$); 64.2 (-CH_2N(CH$_3$)$_2$); 68.0 (-NCH$_2$CH$_2$CH$_2$CH$_2$Si); 86.0, 86.8, 88.4 (-CH_{cim}); 104.7, 106.9 (C$_{cim}$); 129.7, 129.9, 141.1, 157.1, 157.3 (C$_{Ar}$); 168.4 (-CH_{imine}). **^{29}Si-NMR (CDCl$_3$):** δ 1.2 (-CH$_2$Si(CH$_3$)(CH$_2$)$_2$). **Elemental Analysis (%):** Calc. C$_{41}$H$_{78}$Cl$_2$N$_4$RuSi$_3$ (883.33 g/mol): C, 55.75; H, 8.90; N, 6.34; Exp.: C, 55.06; H, 9.46; N, 6.62.

4.2.20. Synthesis of [[Cl(η^6-p-cymene)RuNCPh(o-N)]-G$_2$-[(CH$_2$)$_3$N(CH$_3$)$_2$]$_4$]Cl (20)

Compound **20** was prepared following the same procedure as for compound **13**, using the following reagents: [NCPh(*o*-N)]-G$_2$-[(CH$_2$)$_3$N(CH$_3$)$_2$]$_4$ (32.7 mg, 0.03 mmol) and [Ru(η^6-*p*-cimeno)Cl$_2$]$_2$ (8.9 mg, 0.015 mmol). Compound **20** was identified but not isolated. C$_{69}$H$_{144}$Cl$_2$N$_6$RuSi$_7$ (1426,52 g/mol).**^{1}H-NMR (CD$_3$OD):** δ −0.06 (s, 9H, -CH$_2$Si(CH_3)CH$_2$); 0.00 (s, 24H, -CH$_2$Si(CH_3)$_2$CH$_2$); 0.52 (m overlapping of signals, 34H, -CH_2Si(CH$_3$)CH_2 and -CH_2Si(CH$_3$)$_2$CH_2); 1.04 (m, 3H, -(CH_3)$_2$CH$_{cym}$); 1.14 (m, 3H, -(CH_3)$_2$CH$_{cym}$); 1.46 (m, overlapping of signals, 22H, -CH$_2$CH_2CH$_2$Si(CH$_3$), -SiCH$_2$CH_2CH$_2$Si, -SiCH$_2$CH_2CH$_2$N and NCH$_2$CH$_2$CH_2CH$_2$Si); 2.01 (m, 2H, -NCH$_2$CH_2CH$_2$CH$_2$Si); 2.26 (s, 3H, -CH_{3cym}); 2.37 (m, 24H, -CH$_2$N(CH_3)$_2$); 2.47 (m, 8H, -CH_2N(CH$_3$)$_2$); 2.68 (m, 1H, -(CH$_3$)$_2$CH_{cym}); 4.35 (m, 1H, -NCH_2CH$_2$CH$_2$); 4.59 (m, 1H, -NCH_2CH$_2$CH$_2$); 5.82 (m, 2H, Ar$_{cym}$); 6.07 (m, 1H, Ar$_{cym}$); 6.15 (m, 1H, Ar$_{cym}$); 7.79 (m, 1H, Ar); 8.14 (m, 1H, Ar); 8.21 (m, 1H, Ar); 9.47 (m, 1H, Ar); 8.67 (s, 1H, -CH_{imine}). **^{13}C {^{1}H}-NMR (CD$_3$OD):** δ −4.8 (-CH$_2$Si(CH_3)CH$_2$); −3.1 (-CH$_2$Si(CH_3)$_2$CH$_2$); 13.7 (-SiCH$_2$CH$_2$CH$_2$N(CH$_3$)$_2$); 14.7 (-CH$_2$Si(CH$_3$)$_2$CH_2); 18.4, 18.8, 19.9 (-SiCH$_2$CH$_2$CH$_2$Si); 19.0 (-CH_{3cym}); 21.8 (-NCH$_2$CH$_2$CH_2CH$_2$Si); 22.3 (-SiCH$_2$CH$_2$CH$_2$N); 22.0, 22.4 (-(CH_3)$_2$CH$_{cym}$); 31.5 (-(CH$_3$)$_2$CH_{cym}); 34.8 (-NCH$_2$CH$_2$CH$_2$CH$_2$Si); 45.3 (-CH$_2$N(CH$_3$)$_2$); 64.2 (-CH_2N(CH$_3$)$_2$); 68.0 (-NCH$_2$CH$_2$CH$_2$CH$_2$Si); 86.0, 86.5, 88.4 (-CH_{cym}); 104.7, 106.9 (C$_{cym}$); 129.6, 129.9, 141.0, 157.1, 157.3 (C$_{Ar}$); 168.2 (-CH_{imine}). **^{29}Si-NMR (CDCl$_3$):** δ 1.2 (-CH$_2$Si(CH$_3$)CH$_2$); 1.9 (-CH$_2$Si(CH$_3$)$_2$CH$_2$).

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Appendix A. Supplementary data

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