DOI: 10.1002/ejic.200901187

Preparation and Characterization of Novel Poly(alkylidenamine) Nitrile Ruthenium Metallodendrimers

Manuel G. Jardim,[a] Kari Rissanen,*[b] and João Rodrigues*[a]

Dedicated to Professor Jean-Pierre Sauvage on the occasion of his 65th birthday

Keywords: Ruthenium / Dendrimers / Sandwich complexes / Polynuclear complexes / N ligands

Complete functionalization of *N,N,N′,N′*-[tetrakis(cyanoethyl)-hexamethylenediamine] $[N{\equiv}C(CH_2)_2]_2N(CH_2)_6N[(CH_2)_2-C{\equiv}N]_2$ (**4**) and *N,N,N′,N′*-[tetrakis(cyanoethoxypropyl)hexamethylenediamine] $[N{\equiv}C(CH_2)_2O(CH_2)_3]_2N(CH_2)_6N[(CH_2)_3-O(CH_2)_2C{\equiv}N]_2$ (**7**) with the organometallic moiety $[Ru(\eta^5-C_5H_5)(PPh_3)_2Cl]$ and the five-coordinate *cis*-$[RuCl(dppe)_2][PF_6]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane] was attained with good yield, respectively, by treating the metallofragment with the core in methanol (at room temperature and in presence of $TlPF_6$ as a chloride abstractor) and in 1,2-dichloroethane (under reflux). These novel nitrile-functionalized poly(alkylidenamine) dendrimers peripherally functionalized with the ruthenium moieties $[Ru(\eta^5-C_5H_5)(PPh_3)_2]^+$ and $[RuCl(dppe)_2]^+$ (**8**–**11**) were fully characterized by NMR (^1H, ^{13}C, ^{31}P), TOF-MS and FTIR. The present results represent a step forward in the knowledge of the most adequate synthetic strategy for total coordination of poly(alkylidenamine) nitrile core derivatives to the different ruthenium complex moieties and confirm the versatility of these systems as building blocks in metallodendrimer chemistry.

Introduction

The incorporation of transition-metal complexes into dendritic molecules may lead to new and interesting materials[1] with specific and tunable properties (e.g., catalytic,[2] sensing,[3] biomedical[4] and photo-optical[5]). Coordination chemistry, with its variety of metals and ligands, provides good and straightforward synthetic strategies for the preparation of metallodendrimers.[6] Although amine-functionalized poly(alkylidenamine) derivatives are well-known building blocks for the preparation of dendrimers,[7] the direct use of nitrile poly(alkylidenamine) scaffolds as cores for metallodendrimers remains practically unexplored. Recently, our group prepared new air-stable ruthenium metallodendrimers based on *N,N′*-bis(cyanomethyl)piperazine, *N,N′*-bis[*N′′,N′′′*-bis(cyanoethyl)aminoethyl]piperazine and *N,N,N′,N′*-[tetrakis(cyanoethyl)ethylenediamine] cores functionalized at the surface with $[Ru(\eta^5-C_5H_5)(PPh_3)_2]^+$.[8] This work introduced a novel quantitative method to solidify and chromatographically purify the otherwise semiliquid nitrile-functionalized poly(alkylidenamine) dendrimers and opened the route for the preparation of higher generation poly(alkylidenamine) ruthenium dendrimers with the organometallic moiety $[Ru(\eta^5-C_5H_5)(PPh_3)_2]^+$ at the periphery. To the best of our knowledge, the other few examples in the literature that report the direct use of nitrile poly(alkylidenamine) cores refer to the synthesis of coordination polymers[9] and to the preparation of catalytic dendritic systems formed in situ for Wacker oxidation of terminal olefins bonds.[10]

As part of our studies on the exploitation of the π donor ability of $[Ru(\eta^5-C_5H_5)(PP)]^+$ [PP = $(PPh_3)_2$, dppe, (+)-diop] and $[RuCl(dppe)_2]^+$ for the preparation and characterization of mono-, di- and trinuclear complexes[11] and metallodendrimers[8,12] for nonlinear optical applications using the nitrile group as a coordination bridge to the metallofragments, we wish to report herein our new findings on the preparation and characterization (by NMR, TOF-MS and FTIR) of the first generation of *N,N,N′,N′*-[tetrakis(cyanoethyl)hexamethylenediamine] (**4**) and *N,N,N′,N′*-[tetrakis(cyanoethoxypropyl)hexamethylenediamine] (**7**) dendrimers functionalized with the cationic complexes $[Ru(\eta^5-C_5H_5)(PPh_3)_2]^+$ or $[RuCl(dppe)_2]^+$ at the periphery. Although these metallodendrimers can potentially be used in catalysis, and even in biological applications, synthetic strategies for the preparation of low and high generations of nitrile-functionalized poly(alkylidenamine) ruthenium dendrimers remain practically unexplored.

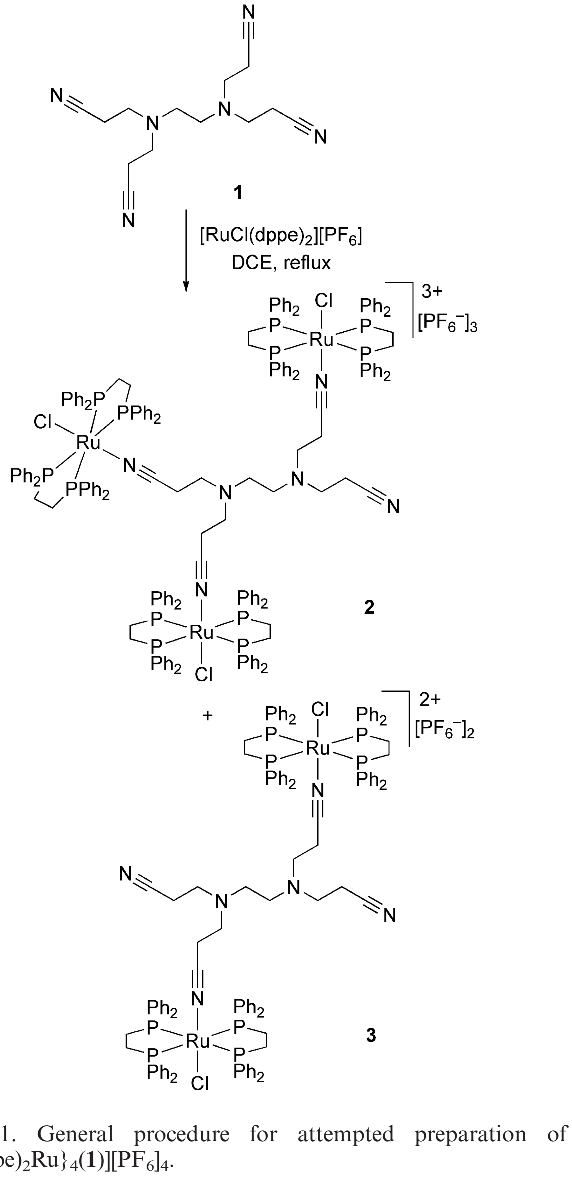
---

[a] Centro de Química da Madeira, LQCMM/MMRG, Departamento de Química da Universidade da Madeira, Campus Universitário da Penteada,
9000-390 Funchal, Portugal
E-mail: joaor@uma.pt
[b] NanoScience Center, Department of Chemistry, University of Jyväskylä,
P. O. Box 35, 40014 JYU, Finland
E-mail: kari.t.rissanen@jyu.fi

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200901187.

Results and Discussion

Following our previous published results,[8] in the present work we started by testing the reaction between *N*,*N*,*N*′,*N*′-[tetrakis(cyanoethyl)ethylenediamine] (**1**) and five-coordinate *cis*-[RuCl(dppe)$_2$][PF$_6$], aiming at the preparation of the tetrakis-ruthenium dendrimer [{Cl(dppe)$_2$Ru}$_4$(**1**)][PF$_6$]$_4$. Several attempts were made to prepare the metallodendrimer that always resulted in a mixture of products impossible to be purified. Mass spectrometry analysis led us to the conclusion that only tricoordinated **2** and dicoordinated **3** were achieved (Scheme 1) with characteristic [M$^+$] peaks at *m*/*z* = 3363 (for **2**) and 2284 (for **3**) (Figure 1). As expected for multicharged metallodendrimers in this mass spectrometry technique, the doubly charged species [{RuCl(dppe)$_2$}$_3$(**1**)(PF$_6$)]$^{2+}$ is visible at *m*/*z* = 1609, resulting from the loss of two counterions from mononitrile **2**. The peak at *m*/*z* = 1205 resulted from fragmentation of mononitrile **2** and dinitrile **3**. The high abundance of complex **3** confirms that this species is already present in the matrix rather than having its origin in simple fragmentation of complex **2**. It is reasonable to assume that the formation of the tetracoordinate product was prevented due to steric hindrance of the bulky metallofragments at the periphery.[12a,13] Although, we were not able to isolate trimeric complex **2**, its formation may represent a new route to higher dendrimer generation. With these results in mind, two synthetic approaches were tested to overcome this problem. The first one was the elongation of the carbon chain between the N–N atoms of the amine core. The carbon chain was increased from two carbon atoms on the *N*,*N*,*N*′,*N*′-[tetrakis(cyanoethyl)ethylenediamine] (**1**) core to six carbon atoms on the *N*,*N*,*N*′,*N*′-[tetrakis(cyanoethyl)-hexamethylenediamine] [N≡C(CH$_2$)$_2$]$_2$N(CH$_2$)$_6$N[(CH$_2$)$_2$-C≡N]$_2$ (**4**) core. To prevent possible steric hindrance in the branches, a second synthesis strategy was used to increase the length of the lateral chains of the core.



Scheme 1. General procedure for attempted preparation of [{Cl(dppe)$_2$Ru}$_4$(**1**)][PF$_6$]$_4$.

Synthesis of Core Ligands *N*,*N*,*N*′,*N*′-[Tetrakis(cyanoethyl)-hexamethylenediamine] [N≡C(CH$_2$)$_2$]$_2$N(CH$_2$)$_6$N[(CH$_2$)$_2$-C≡N]$_2$ (4) and [N≡C(CH$_2$)$_2$O(CH$_2$)$_3$]$_2$N(CH$_2$)$_6$N[(CH$_2$)$_3$-O(CH$_2$)$_2$C≡N]$_2$ (7)

The synthesis of **4** was recently reported[10] while the preparation of this manuscript was under way, although no experimental details or spectroscopic characterization of the compound were given. The new *N*,*N*,*N*′,*N*′-[tetrakis-(cyanoethoxypropyl)hexamethylenediamine] (**7**) was prepared by adapting a reported methodology presented by Jayaraman et al.[14] The precursor [O*t*Bu(C=O)(CH$_2$)$_2$]$_2$-N(CH$_2$)$_6$N[(CH$_2$)$_2$(C=O)O*t*Bu]$_2$ (**5**) was synthesized by Michael addition of *tert*-butyl acrylate, followed by *tert*-butyl ester reduction to give the tetrol [OH(CH$_2$)$_3$]$_2$N-(CH$_2$)$_6$N[(CH$_2$)$_3$OH]$_2$ (**6**). Finally, O-alkylation by a second Michael addition with the use of acrylonitrile led to tetranitrile **7** in good yield (Scheme 2). At the end, new nitrile-functionalized poly(alkylidenamine) dendrimers with an extended inner chain and extended lateral branches were prepared and characterized (compounds **4** and **7**).

Synthesis of Metallodendrimers [{(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Ru}$_4$-(4)][PF$_6$]$_4$ (8), [{(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Ru}$_4$(7)][PF$_6$]$_4$ (9), [{Cl(dppe)$_2$Ru}$_4$(4)][PF$_6$]$_4$ (10) and [{Cl(dppe)$_2$Ru}$_4$(7)][PF$_6$]$_4$ (11)

Following the preparation of **4** and **7**, the synthesis of the first metallodendrimer generation with the two easy-to-make, readily available and stable ruthenium moieties [Ru(η^5-C$_5$H$_5$)(PPh$_3$)$_2$]$^+$ or [RuCl(dppe)$_2$]$^+$ at the periphery was initiated. All reactions involving the preparation of metallodendrimers were carried out under a nitrogen atmosphere by using standard Schlenk techniques. In general terms, the prepared ruthenium dendrimers in the solid state here described are air stable (can be handled in air without particular precautions). These compounds are moderately stable in common organic solvents, but in halogenated sol-

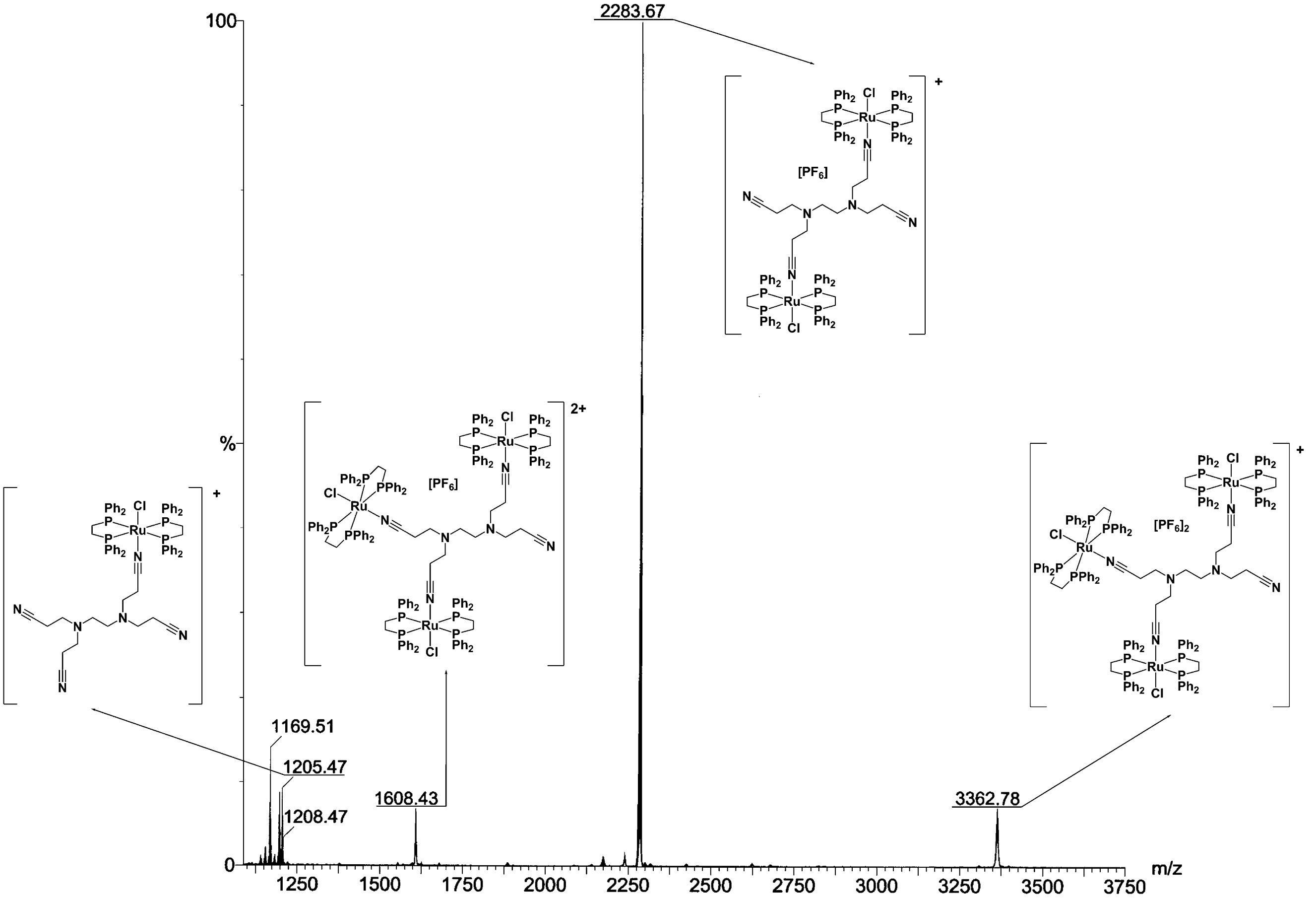


Figure 1. Mass spectrum of mononitrile **2** (m/z = 3363) and dinitrile **3** (m/z = 2284).

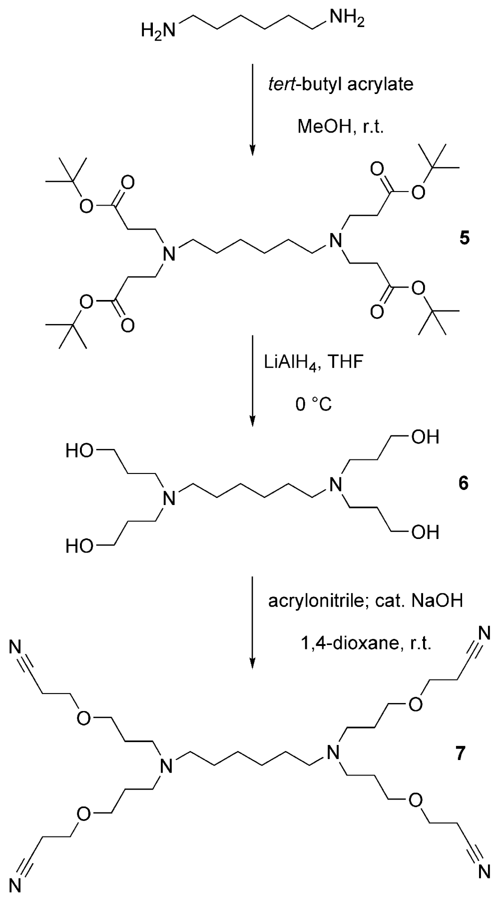
vents compounds **8** and **9** are less stable, preventing lengthy ^{13}C NMR spectroscopic measurements. In spite of the long accumulation time, the ^{13}C NMR experiments for metallodendrimers **10** and **11** did not yield sufficient information to further resolve all the individual carbon resonances.

In a typical experiment, a solution of core **4** or **7** (Scheme 3), [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] (4.5 molar ratio) and $TlPF_6$ (4.5 molar ratio) in methanol was stirred at room temperature. The resulting mixture was filtered, and the solid part was quickly extracted with dichloromethane, which upon solvent evaporation afforded tetrakis-ruthenium dendrimers **8** or **9** in the form of yellow powders (Scheme 3).

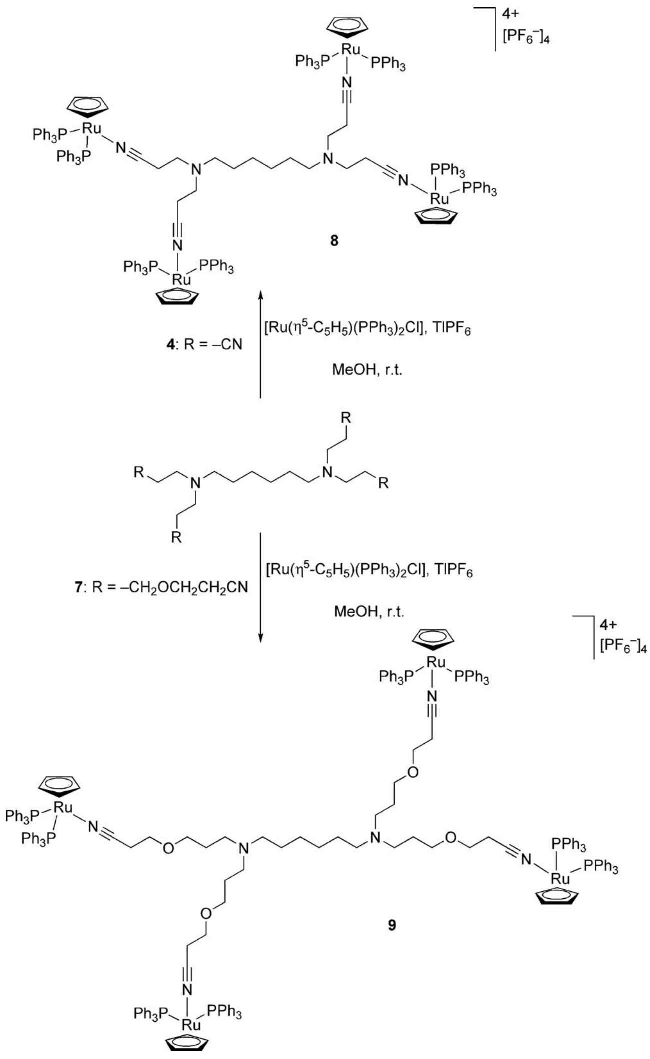
The FTIR spectra of compounds **8** and **9** exhibit the characteristic nitrile band shifted to higher energies by 16 and 17 cm^{-1}, respectively, when compared with the free nitrile. The characteristic bands of the [PF_6]$^-$ counterions are also present (840 and 521 cm^{-1}). The existence of only one nitrile band in the FTIR spectra is indicative that all four branches are coordinated. The ^{31}P NMR spectra of **8** and **9** are similar, both having the expected multiplet at –144.18 ppm ($J_{^{31}P,^{19}F}$ = 712 Hz) for the [PF_6]$^-$ counterion, and only one singlet for the PPh_3 phosphanes ($\delta \approx 42$ ppm for compounds **8** and **9**). Also in the ^{1}H NMR spectrum, only one signal is present for the Cp-ring (around δ = 4.4 ppm). This confirms the equivalence of all ruthenium moieties around the core for both compounds. These results are in good agreement with our previous work[8] where we reported the use of the smaller core *N*,*N*,*N*′,*N*′-[tetrakis(cyanoethyl)ethylenediamine] in the preparation of tetrakis-ruthenium dendrimers. The tetracoordination is also confirmed by TOF-MS (ESI+) analysis, which shows the expected isotopic distribution of peaks around m/z = 3525.94 [M – PF_6]$^+$ and 1691.43 [M – $2PF_6$]$^{2+}$ for **8** and m/z = 1806.99 [M – $2PF_6$]$^{2+}$ for **9**.

For the synthesis of compounds **10** and **11**, we chose to start directly from the five-coordinate *cis*-[RuCl(dppe)$_2$][PF_6] complex, instead of generating it in situ from the complex *cis*-[$RuCl_2$(dppe)$_2$], as this always resulted in the formation of a mixture of unidentified impurities that was not possible to purify. For the general procedure, cores **4** or **7** and *cis*-[RuCl(dppe)$_2$][PF_6] (4.5 molar ratio) were stirred in 1,2-dichloroethane at 90 °C. The resulting mixture was filtered and, after solvent evaporation, afforded yellow powder complexes **10** or **11** (Scheme 4).

The FTIR spectra of compounds **10** and **11** show the nitrile band slightly shifted to higher energies (5 and 8 cm^{-1}, respectively) as well as the bands for the counterion (at 840 and 521 cm^{-1}). The ^{31}P NMR spectra of **10** and **11** are quite similar, both having the expected multiplet at –144.18 ppm ($J_{^{31}P,^{19}F}$ = 712 Hz) for the [PF_6]$^-$ counterion, and one singlet



Scheme 2. Synthesis of *N*,*N*,*N*′,*N*′-[tetrakis(cyanoethoxypropyl)-hexamethylenediamine] (**7**).



Scheme 3. Synthesis of metallodendrimers **8** and **9**.

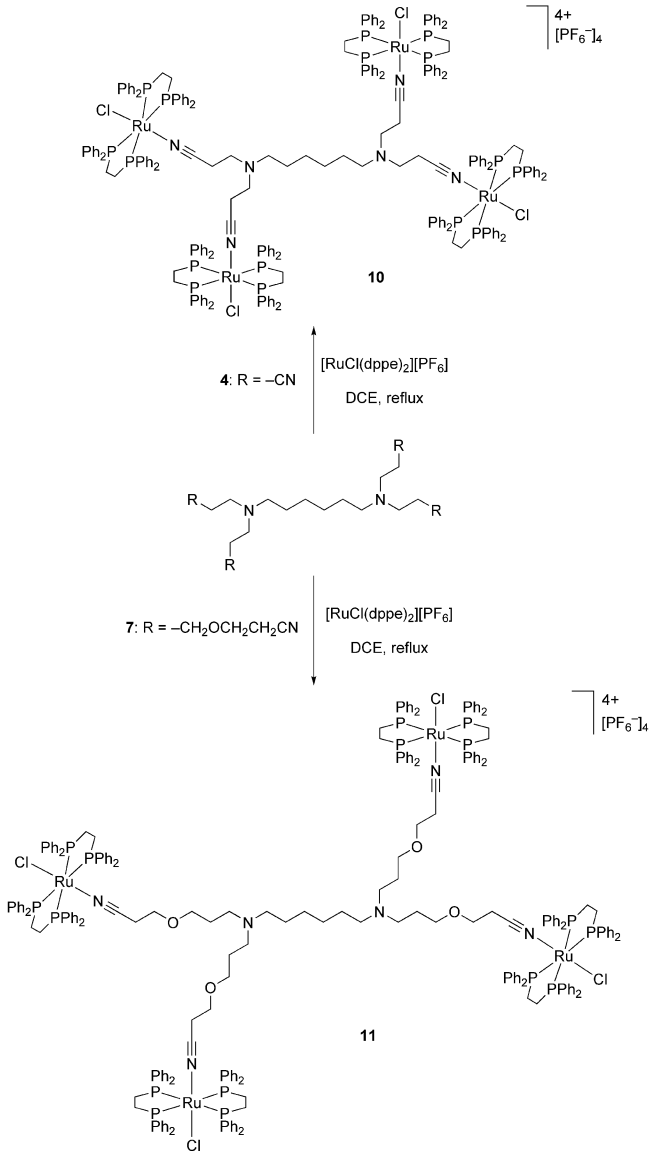
for the $Ph_2PCH_2CH_2PPh_2$ phosphanes (at $\delta \approx 44$ ppm for both compounds), indicating a *trans* geometry around the metal centre for both compounds. To exclude *trans*-$[RuCl_2(dppe)_2]$ (because its chemical shift is similar to that of complexes **10** and **11**) as a reaction product, the dichloridoruthenium complex was added along with compound **10** or **11** and its ^{31}P NMR spectrum was measured; a new peak was visible at ≈ 45 ppm. The *trans* geometry is in accordance with the result found in the literature for the reported compound *trans*-$[Ru(CH_3CN)_2(dppe)_2][OTf]_2$.[15] The expected ratio of protons for the tetracoordinate product (complex/core) was observed in the ^1H NMR spectrum and also confirmed by TOF-MS (ESI+) analysis, which shows the expected isotopic distribution of peaks around $m/z = 4496.88$ $[M - PF_6]^+$ and 2175.78 $[M - 2PF_6]^{2+}$ for **10** and $m/z = 2292.64$ $[M - 2PF_6]^{2+}$ and 1480.48 $[M - 3PF_6]^{3+}$ for **11**.

All our efforts to obtain single crystals suitable for X-ray diffraction from the reported compounds were unsuccessful, probably due to the flexibility of the nitrile poly(alkylidenamine) system.

Conclusions

In this work, new nitrile-functionalized poly(alkylidenamine) dendrimer cores with an extended inner chain and extended lateral branches were prepared {*N*,*N*,*N*′,*N*′-[tetrakis(cyanoethyl)hexamethylenediamine] (**4**) and *N*,*N*,*N*′,*N*′-[tetrakis(cyanoethoxypropyl)hexamethylenediamine] (**7**) cores}. The peripheral functionalization of these dendrimer cores led to the isolation of the first generation of nitrile-functionalized poly(alkylidenamine) ruthenium dendrimers **8**–**11**. These metallodendrimers were obtained in good yield (50–70%) from the organic core by direct reaction with the organometallic moiety $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$ or the five-coordinate *cis*-$[RuCl(dppe)_2][PF_6]$ in methanol (r.t., using $TlPF_6$ to accomplish the substitution of chlorine) or 1,2-dichloroethane (under reflux). The experimental data showed that the metallodendrimers were fully functionalized with the metal complex moieties $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ and $[RuCl(dppe)_2]^+$ in a tetracoordination manner.

This novel series of metallodendrimers based on poly(alkylidenamine) cores belong to a very scarce family of soluble cationic dendrimers (e.g., in DMSO, a common solvent for biological studies) that use the nitrile group as a coordination bridge to the organometallic moieties. This



Scheme 4. Synthesis of metallodendrimers **10** and **11**.

work represents a step forward in the knowledge of the most adequate synthetic strategy for total coordination of poly(alkylidenamine) nitrile core derivatives to different ruthenium complex moieties and confirms the versatility of these systems as building blocks in metallodendrimer chemistry, thus opening the possibility of their use in catalysis or biological applications.[16]

Experimental Section

General: All reactions and manipulations, except for compounds **4**, **5** and **7**, were carried out under a dry nitrogen atmosphere by using standard Schlenk-tube techniques. Prior to use, reagent-grade diethyl ether was distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. Dichloromethane and 1,2-dichloroethane were distilled from calcium hydride under a nitrogen atmosphere and collected prior to use. Absolute methanol was degassed before use. The compounds *cis*-[RuCl(dppe)$_2$][PF$_6$][17] and [Ru(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Cl][11d,18] were prepared according to (modified) literature methods. All others chemicals were purchased from ACROS and used as received. In the preparation of compound **4** we followed the general methodology proposed by Meijer.[19]

Physical Measurements: FTIR spectra were recorded with a Nicolet Avatar 360 FTIR spectrometer, calibrated with polystyrene, in KBr pellets or NaCl cells; only significant bands are cited in the text. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded with a Bruker Avance II$^+$ 400 at 299 K (probe temperature). The chemical shifts (δ) are reported in ppm and referenced to residual solvent peaks for ^{1}H and ^{13}C. ^{31}P NMR is referenced to external 85% H$_3$PO$_4$. The mass spectra (TOF-MS) were recorded with a Micromass LCT spectrometer. Elemental analyses were carried out by using a VariolEL instrument from Elementar Analysensysteme. Melting points were obtained with Electrothermal 9200 equipment.

General Procedure for the Attempted Synthesis of [{Cl(dppe)$_2$-Ru}$_4$(1)][PF$_6$]$_4$: *N*,*N*,*N*′,*N*′-[Tetrakis(cyanoethyl)ethylenediamine] (**1**; 0.03 g, 0.11 mmol) was added to a stirring solution of *cis*-[RuCl(dppe)$_2$][PF$_6$] (0.5 g, 0.46 mmol) in 1,2-dichloroethane (10 mL). The resulting mixture was heated at reflux for 96 h at 85 °C. The solution was filtered, evaporated to dryness under vacuum and washed several times with Et$_2$O. The reddish powder was dissolved in a minimal amount of dichloromethane and precipitated again with Et$_2$O to give a yellowish powder. Attempts were made to purify the final mixture without success. FTIR (KBr): $\tilde{\nu}$ = 2247 (ν_{CN}), 840 and 521(ν_{PF_6}) cm^{-1}. Data for **2**: TOF-MS (ESI+): *m*/*z* = 3362.78 [M – PF$_6$]$^+$, 1608.44 [M – 2PF$_6$]$^{2+}$. Data for **3**: TOF-MS (ESI+): *m*/*z* = 2283.67 [M – PF$_6$]$^+$.

[N≡C(CH$_2$)$_2$]$_2$N(CH$_2$)$_6$N[(CH$_2$)$_2$C≡N]$_2$ (4): At room temperature, 1,6-hexanediamine (1.750 g, 10.00 mmol) was dissolved in H$_2$O (30 mL) and acrylonitrile (2.5 mL, 38.00 mmol) was added in a dropwise fashion. The reaction mixture was warmed up to 48 °C and stirred. After 3 h, the temperature was increased to 80 °C and acrylonitrile (2.5 mL, 38.00 mmol) was added dropwise. After 3 h, the heating was stopped, and the mixture was allowed to cool down. The volatiles were removed by vacuum to afford **4** as a colourless oil. Yield: 4.739 g (96%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.85 (t, $J_{H,H}$ = 6.8 Hz, 8 H), 2.54 (t, $J_{H,H}$ = 14.1 Hz, 4 H), 2.47 (t, $J_{H,H}$ = 6.8 Hz, 8 H), 1.46 (m, 4 H), 1.34 (m, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 118.8 (N*C*CH$_2$-), 53.3, 49.6, 27.3, 26.8, 16.9 ppm. FTIR (liquid): $\tilde{\nu}$ = 2247.5 (ν_{CN}) cm^{-1}. TOF-MS (ESI+): *m*/*z* = 329.23 [M + H]$^+$, 351.21 [M + Na]$^+$.

[O*t*Bu(C=O)(CH$_2$)$_2$]$_2$N(CH$_2$)$_6$N[(CH$_2$)$_2$(C=O)O*t*Bu]$_2$ (5): To a solution of 1,6-hexanediamine (1.00 g, 8.61 mmol) in MeOH (10 mL) was dropwise added *tert*-butyl acrylate (6.5 mL, 44.8 mmol). The mixture was stirred for 16 h and the volatiles were removed in vacuo to give a white solid. No further purification was necessary. Yield: 3.924 g (85%). M.p. 56–57 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.71 (t, $J_{H,H}$ = 14.7 Hz, 8 H), 2.43–2.30 (m, 8 H + 4 H), 1.49–1.39 (m, 36 H + 4 H), 1.26 (m, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.1 (R-*C*=O), 80.1 [-O-*C*(CH$_3$)$_3$], 53.8, 49.4, 33.7, 28.1, 27.4 ppm. TOF-MS (ESI+): *m*/*z* = 629.45 [M + H]$^+$, 651.48 [M + Na]$^+$.

[OH(CH$_2$)$_3$]$_2$N(CH$_2$)$_6$N[(CH$_2$)$_3$OH]$_2$ (6): To a suspension of LiAlH$_4$ (1.072 g, 28.20 mmol) in THF (20 mL) at 0 °C was added a solution of **5** (3.700 g, 5.90 mmol) in THF (15 mL) dropwise. The reaction mixture was stirred at 0 °C for 1 h, brought to room temperature and stirred for another hour. The reaction mixture was again cooled to 0 °C and quenched with ice. The suspension was passed through a plug of Celite 545, and the filtrate was dried and concentrated to obtain **6** as a colourless liquid. Yield: 1.922 g (94%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.58 (t, 8 H), 2.49 (t, 8

H), 2.30 (t, 4 H), 1.60 (m, 8 H), 1.38 (br., 4 H), 1.22 (br., 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.3, 53.9, 52.8, 28.5, 27.1, 26.4 ppm. TOF-MS (ESI+): m/z = 349.27 $[M + H]^+$, 371.29 $[M + Na]^+$.

$[N{\equiv}C(CH_2)_2O(CH_2)_3]_2N(CH_2)_6N[(CH_2)_3O(CH_2)_2C{\equiv}N]_2$ (7): Acrylonitrile (1.7 mL, 25.60 mmol) was added to a mixture of **6** (1.781 g, 5.10 mmol) and aqueous NaOH (40%) (0.21 mL) in 1,4-dioxane (5 mL). The reaction mixture was stirred for 16 h at room temperature. The solvent was removed to give a brownish residue. This residue was dissolved in $CHCl_3$ (15 mL), washed with aqueous HCl (1 M), 5% of aqueous NaOH and brine and dried thoroughly to afford **7** as a colourless liquid. Yield: 2.591 g (90%). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.61 (t, 8 H), 3.50 (t, 8 H), 2.57 (t, 8 H), 2.46 (t, 8 H), 2.35 (t, 4 H), 1.68 (m, 8 H), 1.39 (m, 4 H), 1.25 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.1 ($NCCH_2$-), 69.3, 65.1, 54.0, 50.3, 27.2, 18.7 ppm. FTIR (liquid): $\tilde{\nu}$ = 2251 (ν_{CN}) cm^{-1}. TOF-MS (ESI+): m/z = 561.28 $[M]^+$.

$[\{(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru\}_4(4)][PF_6]_4$ (8): $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$ (0.325 g, 0.45 mmol), (**4**) (0.035 g, 0.11 mmol) and $TlPF_6$ (0.205 g, 0.59 mmol) were introduced with MeOH (30 mL) into a Schlenk tube. The resulting orange suspension was stirred at room temperature for 113 h. The yellow suspension was filtered and dried under vacuum. Then, the yellow solid was quickly extracted with dichloromethane to prevent decomposition. Solvent removal afforded a bright yellow powder. Pure **8** was obtained after washing the powder with Et_2O (3 × 15 mL). Yield: 0.279 g (74%). M.p. 196–197 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–6.90 (m, 24 H + 48 H + 48 H, PPh_3), 4.46 (s, 20 H, C_5H_5), 2.53 (br., 8 H) 2.39 (br., 16 H), 2.22 (br., 8 H), 1.20 (br., 8 H; overlapped with the solvent peaks) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 41.8 (s, PPh_3), –144.18 (m, $J_{^{31}P,^{19}F}$ = 712 Hz, PF_6) ppm. FTIR (KBr): $\tilde{\nu}$ = 2263 (ν_{CN}), 840 and 521(ν_{PF_6}) cm^{-1}. TOF-MS (ESI+): m/z = 3525.94 $[M - PF_6]^+$, 1691.43 $[M - 2PF_6]^{2+}$. $C_{182}H_{168}F_{24}N_6P_{12}Ru_4\cdot1/2CH_2Cl_2$ (3713.71): calcd. C 59.02, H 4.59, N 2.26; found C 58.99, H 4.61, N 2.34.

$[\{(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru\}_4(7)][PF_6]_4$ (9): $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$ (0.408 g, 0.56 mmol) and **7** (0.070 g, 0.12 mmol) were introduced with MeOH (35 mL) into a Schlenk tube. To the orange suspension was added $TlPF_6$ (0.205 g, 0.59 mmol), and the mixture was stirred at room temperature for 41 h. The yellow suspension was filtered and dried under vacuum. Then, the yellow product was quickly extracted with dichloromethane. Solvent removal gave a bright yellow powder. Pure **9** was obtained after washing the powder with Et_2O (3 × 15 mL). Yield: 0.307 g (63%). M.p. 125 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–6.90 (m, 24 H + 48 H + 48 H, PPh_3), 4.44 (s, 20 H, C_5H_5), 3.31 (br., 8 H + 8 H), 2.84 (br., 8 H + 4 H), 1.28 (br., 4 H + 4 H) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 41.6 (s, PPh_3), –144.18 (m, $J_{^{31}P,^{19}F}$ = 712 Hz, PF_6) ppm. FTIR (KBr): $\tilde{\nu}$ = 2268 (ν_{CN}), 840 and 521(ν_{PF_6}) cm^{-1}. TOF-MS (ESI+): m/z = 1806.99 $[M - 2PF_6]^{2+}$. $C_{194}H_{192}F_{24}N_6O_4P_{12}Ru_4\cdot3/5CH_2Cl_2$ (3954.52): calcd. C 59.10, H 4.92, N 2.13; found C 58.94, H 4.93, N 2.32.

$[\{Cl(dppe)_2Ru\}_4(4)][PF_6]_4$ (10): To a solution of *cis*-$[RuCl(dppe)_2][PF_6]$ (0.670 g, 0.62 mmol) in 1,2-dichloroethane (10 mL) was dropwise added **4** (0.045 g, 0.14 mmol) dissolved in 1,2-dichloroethane (10 mL). The resulting red solution was heated at reflux for 96 h. The solution was filtered, evaporated to dryness under vacuum and washed several times with Et_2O. The reddish powder was dissolved in a minimal amount of dichloromethane and reprecipitated with Et_2O to give a yellowish powder. Yield: 0.148 g (47%). M.p. 226 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–6.50 (m, 160 H, PPh_2), 2.79 (br., 32 H, PCH_2CH_2P), 1.95 (br., 4 H), 1.74 (br., 16 H), 1.26 (br., 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 132.6, 130.2, 128.8, 127.8, 52.2, 47.9, 29.5, 27.6, 18.7 ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 44.1 (s, PPh_2), –144.18 (m, $J_{^{31}P,^{19}F}$ = 712 Hz, PF_6) ppm. FTIR (KBr): $\tilde{\nu}$ = 2252 (ν_{CN}), 840 and 521(ν_{PF_6}) cm^{-1}. TOF-MS (ESI+): m/z = 4496.88 $[M - PF_6]^+$, 2175.78 $[M - 2PF_6]^{2+}$. $C_{226}H_{220}Cl_4F_{24}N_6P_{20}Ru_4\cdot1/4CH_2Cl_2$ (4662.97): calcd. C 58.28, H 4.77, N 1.80; found C 58.19, H 4.85, N 1.92.

$[\{Cl(dppe)_2Ru\}_4(7)][PF_6]_4$ (11): *cis*-$[RuCl(dppe)_2][PF_6]$ (0.525 g, 0.49 mmol) in 1,2-dichloroethane (30 mL) was added to compound **7** (0.063 g, 0.11 mmol) by cannula. The resulting red solution was heated at reflux for 65 h. The solution was filtered, evaporated to dryness under vacuum and washed several times with Et_2O. The reddish powder was dissolved in a minimal amount of dichloromethane and reprecipitated with Et_2O to give a yellowish powder. Yield: 0.319 g (70%). M.p. 174–176 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–6.50 (m, 160 H, PPh_2), 3.41 (br., 8 H), 2.93 (br., 8 H), 2.71 (br., 32 H, PCH_2CH_2P), 1.85 and 1.76 (br., 14 H), 1.21 (br., 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 132.3, 130.6, 128.7, 127.9, 69.0, 64.9, 54.0, 50.7, 29.4, 21.8 ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 44.1 (s, PPh_2), –144.18 (m, $J_{^{31}P,^{19}F}$ = 712 Hz, PF_6] ppm. FTIR (KBr): $\tilde{\nu}$ = 2259 (ν_{CN}), 840 and 521(ν_{PF_6}) cm^{-1}. TOF-MS (ESI+): m/z = 2292.64 $[M - 2PF_6]^{2+}$, 1480.48 $[M - 3PF_6]^{3+}$. $C_{238}H_{244}Cl_4F_{24}N_6O_4P_{20}Ru_4\cdot1.7CH_2Cl_2$ (5018.44): calcd. C 57.37, H 4.97, N 1.67; found C 57.39, H 4.95, N 1.62.

Supporting Information (see footnote on the first page of this article): Spectroscopic data are available for compounds **4**–**11**.

Acknowledgments

This research was partially supported by Fundação para a Ciência e a Tecnologia (FCT) through the research project PTDC/QUI/64202/2006. J.R. gratefully acknowledges the Socrates/Erasmus Program for financial support. K.R. acknowledges the Academy of Finland for a research grant (Project no. 212588). The NMR and mass spectrometers are part of the Portuguese National Nuclear Magnetic Resonance and Mass Spectrometry Networks (Contracts PTNMR-REDE/1517/RMN/2005 and RNEM-REDE/1508/REM/2005) and were purchased in the framework of the National Programme for Scientific Re-equipment, with funds from POCI 2010 (FEDER) and the FCT. We gratefully acknowledged continuing support of our work by CS Madeira. The authors are grateful to the referees who gave detailed and valuable comments on the manuscript.

---

[1] See, for example: a) O. Rolland, C. O. Turrin, A.-M. Caminade, J.-P. Majoral, *New J. Chem.* **2009**, *33*, 1809–1824; b) C. Ornelas, J. Ruiz, D. Astruc, *Organometallics* **2009**, *28*, 2716–2723; c) S.-H. Hwang, C. D. Shreiner, C. N. Moorefield, G. R. Newkome, *New J. Chem.* **2007**, *7*, 1192–1217; d) D.-Lin, T. Aida, *Prog. Polym. Sci.* **2005**, *30*, 403–422; e) E. C. Wiener, V. V. Narayanan in *Advances in Dendritic Macromolecules* (Ed.: G. R. Newkome), Elsevier, Kidlington, Oxford, UK, **2002**.

[2] a) C. Ornelas, J. R. Aranzaes, C. Belin, D. Astruc, *J. Am. Chem. Soc.* **2009**, *131*, 590–601; b) D. Astruc, C. Ornelas, J. Ruiz, *Acc. Chem. Res.* **2008**, *41*, 841–856; c) E. Jesus, J. C. Flores, *Ind. Eng. Chem. Res.* **2008**, *47*, 7968–7981; d) C. Ornelas, J. R. Aranzaes, L. Salmon, D. Astruc, *Chem. Eur. J.* **2008**, *14*, 50–64; e) D. Méry, D. Astruc, *Coord. Chem. Rev.* **2006**, *250*, 1965–1979; f) R. van Heerbeeck, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Rev.* **2002**, *102*, 3717–3756.

[3] a) G. Zaupa, P. Scrimin, L. J. Prins, *J. Am. Chem. Soc.* **2008**, *130*, 5699–5709; b) X. Shi, I. Lee, J. R. Baker Jr., *J. Mater. Chem.* **2008**, *18*, 586–593; c) C. Ornelas, J. R. Aranzaes, E. Cloutet, S. Alves, D. Astruc, *Angew. Chem. Int. Ed.* **2007**, *46*,

872–877; d) A. Trinchi, T. H. Muster, *Supramol. Chem.* **2007**, *19*, 431–445.

[4] a) E. J. Jurez-Perez, C. Vinas, F. Teixidor, R. Nunez, *Organometallics* **2009**, *28*, 5550–5559; b) X. Shi, S. Wang, S. Meshinchi, M. E. Van Antwerp, X. Bi, I. Lee, J. R. Baker Jr., *Small* **2007**, *3*, 1245–1252; c) H.-B. Yang, A. M. Hawkridge, S. D. Huang, N. Das, S. D. Bunge, D. C. Muddiman, P. J. Stang, *J. Am. Chem. Soc.* **2007**, *129*, 2120–2129; d) C. Lee, J. A. Mac Kay, J. M. J. Fréchet, F. Szoka, *Nat. Biotechnol.* **2005**, *23*, 1517–1526; e) U. Boas, P. M. H. Heegarard, *Chem. Soc. Rev.* **2004**, *33*, 43–63; f) M. W. Grinstaff, *Chem. Eur. J.* **2002**, *8*, 2838–2846; g) S. E. Stiriba, H. Frey, R. Haag, *Angew. Chem. Int. Ed.* **2002**, *41*, 1329–1334; h) M. J. Cloninger, *Curr. Opin. Chem. Biol.* **2002**, *6*, 742–748; i) K. Sadler, J. P. Tam, *J. Biotechnol.* **2002**, *90*, 195–205; j) C. Kojima, K. Kono, K. Maruyama, T. Takagishi, *Bioconjugate Chem.* **2000**, *11*, 910–917.

[5] a) C. E. Powell, M. P. Cifuentes, M. G. Humphrey, A. C. Willis, J. P. Morrall, M. Samoc, *Polyhedron* **2007**, *26*, 284–289; b) R. L. Roberts, T. Schwich, T. C. Corkery, C. E. Powell, M. P. Cifuentes, K. A. Green, J. D. Farmer, P. J. Low, T. B. Marder, M. Samoc, M. G. Humphrey, *Adv. Mater.* **2009**, *21*, 2318–2322 and references cited therein.

[6] a) F. Vögtle, G. Richardt, N. Werner, *Dendrimer Chemistry: Concepts, Syntheses, Properties, Applications*, Wiley-VCH, Weinheim, **2009**; b) J. M. J. Fréchet, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4782–4787; c) G. R. Newkome, E. He, C. N. Moorefield, *Chem. Rev.* **1999**, *99*, 1689–1746.

[7] a) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons: Concepts, Synthesis and Applications*, Wiley-VCH, Weinheim, **2001**; b) I. Cuadrado, M. Morán, C. M. Casado, B. Alonso, F. Lobete, B. García, M. Ibisate, J. Losada, *Organometallics* **1996**, *15*, 5278–5280.

[8] C. Ornelas, V. Vertlib, J. Rodrigues, K. Rissanen, *Eur. J. Inorg. Chem.* **2006**, 47–50.

[9] K. S. Min, M. P. Suh, *J. Am. Chem. Soc.* **2000**, *122*, 6834–6840.

[10] E. A. Karakhanov, A. L. Maximov, B. N. Tarasevich, V. A. Skorkin, *J. Mol. Catal. A* **2009**, *297*, 73–79.

[11] a) M. H. Garcia, J. C. Rodrigues, A. R. Dias, M. F. M. Piedade, M. T. Duarte, M. P. Robalo, N. Lopes, *J. Organomet. Chem.* **2001**, *632*, 133–144; b) W. Wenseleers, E. Goovaerts, M. H. Garcia, M. P. Robalo, P. J. Mendes, J. C. Rodrigues, A. R. Dias, *J. Mater. Chem.* **1998**, *4*, 925–930; c) A. R. Dias, M. H. Garcia, J. C. Rodrigues, J. Petersen, T. Bjørnholm, T. Geisler, *J. Mater. Chem.* **1995**, *5*, 1861–1865; d) A. R. Dias, M. H. Garcia, J. C. Rodrigues, M. L. H. Green, S. M. Kuebler, *J. Organomet. Chem.* **1994**, *475*, 241–245; e) A. R. Dias, M. H. Garcia, P. J. Mendes, M. P. Robalo, J. C. Rodrigues, *Trends Organomet. Chem.* **1994**, *1*, 335–343; f) L. Russo, J. Figueira, J. Rodrigues, K. Rissanen, *Acta Crystallogr., Sect. E* **2006**, *62*, m1154–m1155; g) L. Russo, J. Figueira, J. Rodrigues, K. Rissanen, *Acta Crystallogr., Sect. E* **2006**, *62*, m699–m701; h) C. Ornelas, C. Gandum, J. Mesquita, J. Rodrigues, M. H. Garcia, N. Lopes, M. P. Robalo, K. Nättinen, K. Rissanen, *Inorg. Chim. Acta* **2005**, *358*, 2482–2488; i) C. Vertlib, J. Figueira, J. Mesquita, J. Rodrigues, K. Nättinen, K. Rissanen, *Eur. J. Inorg. Chem.* **2007**, 1920–1924.

[12] a) C. Ornelas, J. Ruiz, J.-C. Blais, J. Rodrigues, D. Astruc, *Organometallics* **2004**, *23*, 4271–4276; b) D. Méry, L. Plault, C. Ornelas, J. Ruiz, S. Nlate, D. Astruc, J.-C. Blais, J. Rodrigues, S. Cordier, K. Kirakci, C. Perrin, *Inorg. Chem.* **2006**, *45*, 1156–1167; c) C. Ornelas, J. Ruiz, J. Rodrigues, D. Astruc, *Inorg. Chem.* **2008**, *47*, 4421–4428.

[13] S. K. Hurst, M. P. Cifuentes, M. G. Humphrey, *Organometallics* **2002**, *21*, 2353–2355.

[14] T. R. Krishna, N. Jayaraman, *J. Org. Chem.* **2003**, *68*, 9694–9704.

[15] J. F. Bickley, A. La Pensée, S. J. Higgins, C. A. Stuart, *Dalton Trans.* **2003**, 4663–4668.

[16] During the preparation of this manuscript, G. S. Smith et al. reported the in vitro anticancer activity size dependency of neutral multinuclear ruthenium complexes based on a poly(propylenamine) scaffold, which prompts us to expect in the near future a growing interest in the exploitation of this type of metallodendrimers as anticancer agents. See: P. Govender, N. C. Antonels, J. Mattsson, A. K. Renfrew, P. J. Dyson, J. R. Moss, B. Therrien, G. S. Smith, *J. Organomet. Chem.* **2009**, *694*, 3470–3476.

[17] B. Chin, A. J. Lough, R. H. Morris, C. T. Schweitzer, C. D'Agostino, *Inorg. Chem.* **1994**, *33*, 6278–6288.

[18] M. I. Bruce, N. J. Windsor, *Aust. J. Chem.* **1977**, *30*, 1601–1604.

[19] E. M. M. van der Berg, E. W. Meijer, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1308–1312.

Received: December 8, 2009
Published Online: March 3, 2010