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Ruthenium Metallodendrimers Based on Nitrile-Functionalized Poly(alkylidene imine)s

Cátia Ornelas,[a] Viatcheslav Vertlib,[a] João Rodrigues,*[a] and Kari Rissanen*[b]

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The preparation of the first- and second-generation of nitrile-functionalized poly(alkylidene imine) dendrimers with the organometallic ruthenium complex [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] peripherally attached is described. The reaction of *N*,*N*′-bis-(cyanomethyl)piperazine (**1**), *N*,*N*′-bis[*N*′′,*N*′′′-bis(cyanoethyl)aminoethyl]piperazine (**2**), or *N*,*N*,*N*′,*N*′-tetrakis(cyanoethyl)ethylenediamine (**3**) with [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] (**4**) in the presence of $TlPF_6$ gives the new air-stable ruthenium metallodendrimers **5**, **6**, and **7**, respectively. These stable metallodendrimers are easily prepared and represent a novel quantitative method to solidify and chromatographically purify the otherwise semi-liquid nitrile-functionalized poly(alkylidene imine) dendrimers. The compounds were fully characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and mass spectrometry. These dendrimers represent the first example of the utilization of nitrile-functionalized poly(alkylidene imine)s as cores in the preparation of metallodendrimers.

Introduction

Coordination-chemistry-based dendrimers can be easily prepared by straightforward synthetic methods by an appropriate choice of metals and ligands.[1] One of the most promising aspects of metallodendrimers[1–4] is their applicability as renewable metallodendritic catalysts,[5–7] as well as nanoscale molecular materials[8] with unusual physical or optical properties to be used as nonlinear optics (NLO) materials.[9–12]

Even though poly(propylene imine) derivatives are well known building blocks for the preparation of dendrimers,[13] the direct use of nitrile-functionalized poly(alkylidene imine) as a core for the preparation of metallodendrimers has not been reported prior to this work. In a previous work[14] we succeeded in the preparation of hexa- and nonaruthenium star-shaped complexes by using [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] as the organometallic ruthenium reagent. The same reasoning was followed in this work and we explored the use of nitrile-functionalized poly(alkylidene imine)s (generation 0 and 1) for the coordination to the organometallic fragment [Ru(η^5-C_5H_5)(PPh_3)$_2$]. The aim was the development of novel methods for the preparation of new nanoscopic molecular materials (metallodendrimer-based) with particular physical (NLO) and/or chemical properties (catalytic activity).

[a] Centro de Química da Madeira, LQCMM, Departamento de Química da Universidade da Madeira, Campus Universitário da Penteada,
9000-390 Funchal, Portugal
[b] NanoScience Center, Department of Chemistry, University of Jyväskylä,
P. O. Box 35, 40014 Jyväskylä, Finland

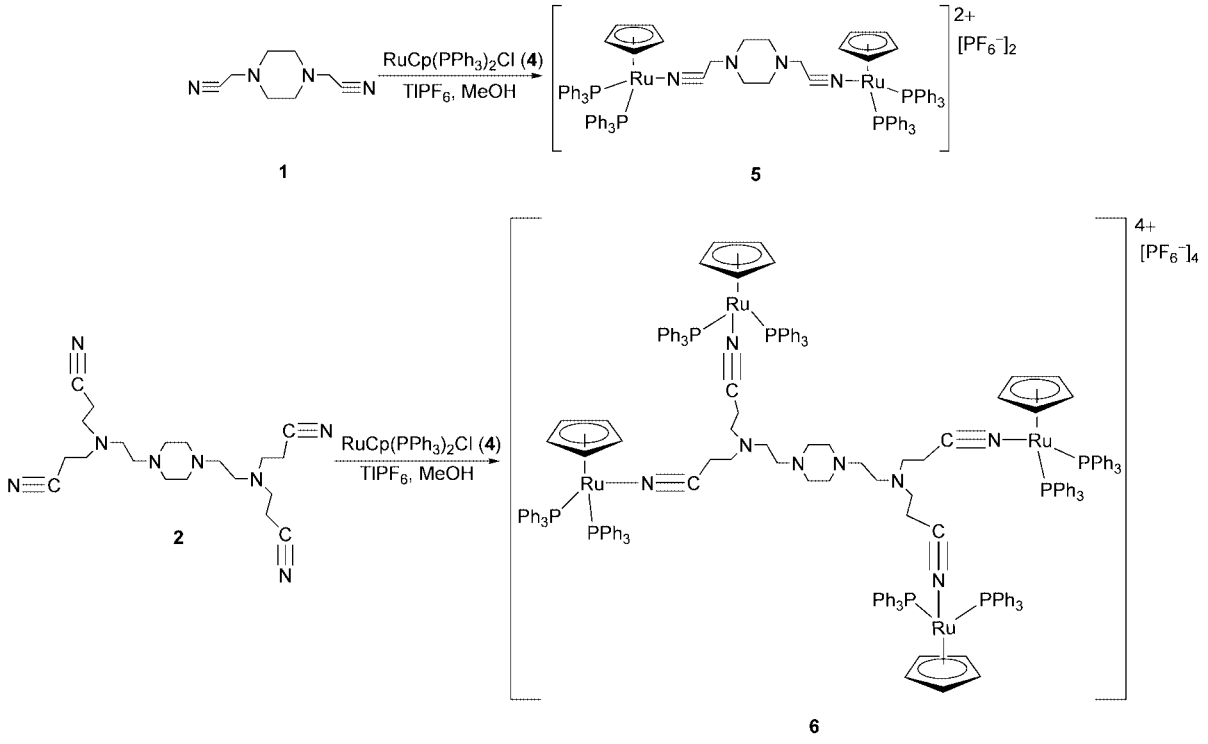
Results and Discussion

The core nitrile-functionalized poly(alkylidene imine)s *N*,*N*′-bis(cyanomethyl)piperazine (**1**), *N*,*N*′-bis[*N*′′,*N*′′′-bis-(cyanoethyl)aminoethyl]piperazine (**2**), and *N*,*N*,*N*′,*N*′-tetrakis(cyanoethyl)ethylenediamine (**3**) were obtained in good yields by reaction of piperazine with chloroacetonitrile (**1**). The precursor amine for **2** was obtained by reduction of nitrile **1** with $LiAlH_4$. The piperazine and ethylenediamine were then treated with acrylonitrile under classic Michael reaction conditions.[15] The exact synthetic details of the preparation of **1**–**3** will be reported elsewhere.

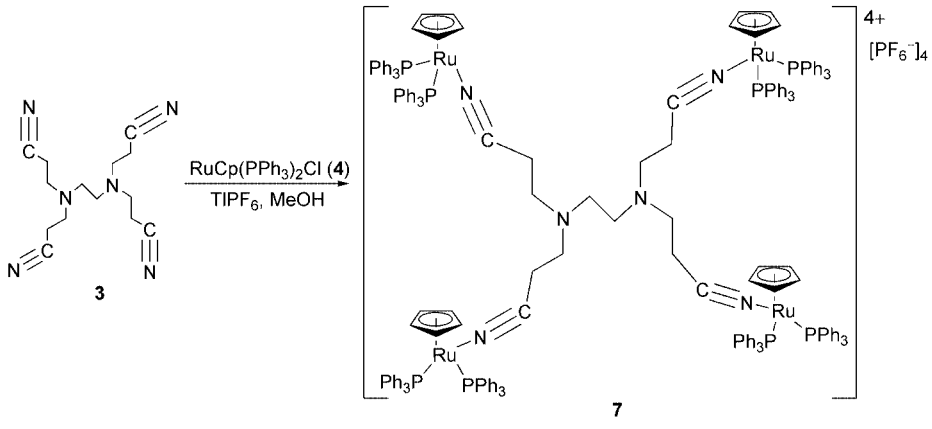
These organic cores were quantitatively coordinated to the ruthenium reagent [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] (**4**) by substitution of chloride and coordination to the nitrile nitrogen, using a slight excess of $TlPF_6$ in methanol, resulting in the bis- and tetrakisruthenium-bonded dendrimers (Schemes 1 and 2).

These organometallic dendrimers were isolated in good yields as air-stable, yellow powders and were characterized by UV/Vis, IR, and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and mass spectrometry.

The IR spectra of **5**, **6**, and **7** show, besides the characteristic band of the PF_6^- counterion at 840 and 521 cm^{-1}, the nitrile band shifted to higher energies by 5, 14, and 21 cm^{-1}, respectively, when compared with the free nitrile, thus indicating similar coordination of all termini of the cores to the ruthenium fragment. These results are in accordance with the ^{1}H NMR spectra, which show only one signal for CH_2CN shifted downfield and good relation/integrations between the protons of the ruthenium fragment and the protons of the cores. The ^{13}C NMR spectra also show the expected signals, except for the nitrile carbon, which could



Scheme 1. First- and second-generation ruthenium metallodendrimers with piperazine cores.



Scheme 2. A ruthenium metallodendrimer with an imine core.

not be detected due to slow relaxation. The appearance of only one Cp-ring signal at around δ = 4.5 ppm in the ^{1}H NMR spectrum and only one phosphorus signal in the ^{31}P NMR spectrum ($\delta \approx 42$ ppm) for all products is due to the equivalence of the ruthenium fragments coordinated to the cores and confirms the bis and the tetra coordination.

Clean mass spectra were obtained for all products, showing the characteristic [M$^+$] peaks at m/z = 1691 (**5**), 3583 (**6**, Figure 1), and 3471 (**7**) and some peaks of typical fragmentations of the molecule in this technique (TOF-MS; see Experimental Section).

All the UV/Vis electronic spectra of the ruthenium dendrimers, recorded in ca. 10^{-5} M solutions of CH_2Cl_2, show a shoulder at around 351 nm with ε values in the range 0.7–1×10^4 M^{-1} cm^{-1}. This behavior is probably due to a metal-to-ligand charge-transfer (MLCT) transition, since a similar transition is absent both in [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] and in the uncoordinated cores.

Although there is not sufficient literature data for 1:4 complex salts,[16] the conductivity measurements, together with the spectroscopic data, indicate that the assumption of 1:2 and 1:4 complex salts is correct.

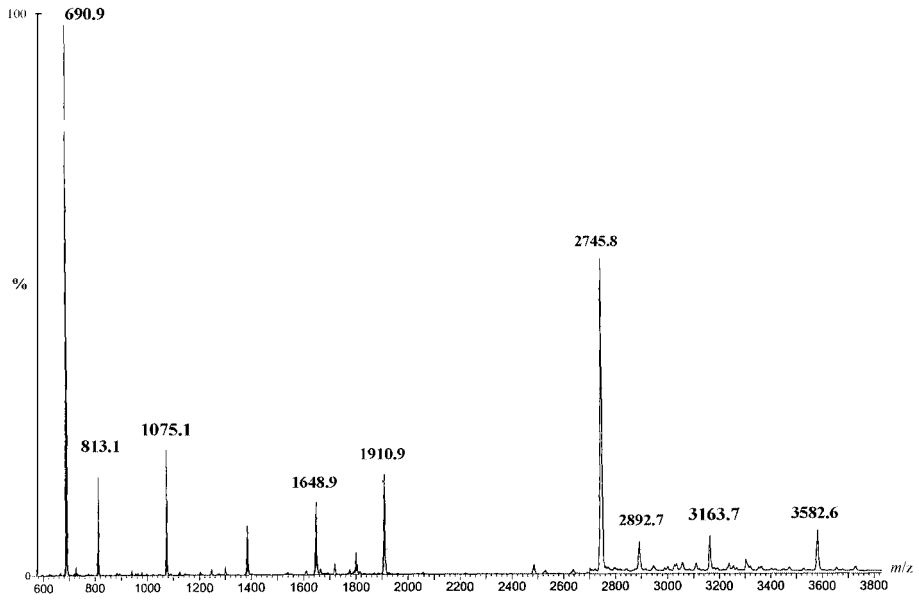


Figure 1. Mass spectrum of compound **6** showing the [M^+] peak at m/z = 3583.

Several attempts to obtain crystals of these metallodendrimers for the elucidation of their structures in the solid state failed, producing only microcrystals unsuitable for X-ray diffraction.

Conclusions

We have reported the preparation and characterization of the first- and second-generation poly(alkylidene imine) ruthenium dendrimers using nitrile-functionalized poly(alkylidene imine)s as cores and the organometallic fragment [Ru(η^5-C_5H_5)(PPh_3)$_2$] at the periphery. The easy preparation of these stable metallodendrimers represents a novel quantitative method to solidify and chromatographically purify the otherwise amorphous or semi-liquid nitrile-functionalized poly(alkylidene imine) dendrimers. The chromatographic purification of dendritic compounds is still rare and our method could be of help for purification of other dendritic nitriles. Our efforts are currently focused on the synthesis of higher generations of metallodendrimers and on the use of different metallic fragments to obtain dendrimers with different properties and applications.

Experimental Section

General: All experiments were carried out under vacuum or nitrogen atmosphere by use of standard Schlenk techniques. With the exception of absolute methanol, which was used without further purification and degassed before use, all the solvents used were dried according to the usual published methods[17] and distilled prior to use. The compound [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] (**4**) was prepared and characterized as described in the literature.[18,19]

Physical Measurements: The UV/Vis spectra were recorded with a GBC-Cintra 40, UV/Vis spectrometer using 1-cm optical-path quartz cells with freshly prepared solutions of approximately 10^{-5} M concentration in CH_2Cl_2. The mass spectra (TOF-MS) were recorded on a Micromass LCT. FT-IR spectra were recorded with a Nicolet Avatar 360 FTIR spectrometer, calibrated with polystyrene, as KBr pellets; only significant bands are cited in the text. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AM500 spectrometer at 500.13, 125.77, and 202.44 MHz, respectively, at 293.15 K (probe temperature). The ^{1}H chemical shifts (δ), reported in parts per million (ppm) downfield, are referenced to residual chloroform (δ = 7.24 ppm). The ^{13}C{^{1}H} chemical shifts were reported in ppm relative to the carbon resonance of the deuterated NMR solvent ($CDCl_3$: δ = 77.00 ppm). The ^{31}P{^{1}H} NMR spectra are reported in ppm downfield from external 85% H_3PO_4 (δ = 0.00 ppm). The elemental analysis of the complexes did not give satisfactory results after several tries and is not reported. The probable reasons for these irreproducible results are the evaporation of the possible lattice solvent molecules (MeOH, CH_2Cl_2, $CHCl_3$, or diethyl ether) and/or the adsorption/desorption of moisture. Conductivity measurements were made at 273.15 K on freshly made 10^{-3} M solutions of the complexes in nitromethane using a CRISON-microCM 2200. The cell constant was determined by measuring the resistance of an aqueous solution of KCl (0.0100 M, σ = 0.001413 Ω^{-1} cm^{-1} at 273.15 K). Molar conductivities (Λ_M) are given in units of Ω^{-1} cm^2 mol^{-1}. The accepted ranges for 1:2- and 1:4-type electrolytes under these conditions are 100–160 and 290–330 Ω^{-1} cm^2 mol^{-1}, respectively.[16]

Synthesis of 5: [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] (**4**; 0.4509 g, 0.620 mmol) and the dinitrile **1** (0.051 g, 0.310 mmol) were introduced with MeOH (30 mL), under nitrogen, into a flame-dried Schlenk flask. $TlPF_6$ (0.250 g, 0.713 mmol) was added and, after stirring the mixture for 13 h, the solvent was removed under vacuum. The product was extracted with CH_2Cl_2 and, after filtration, the solvent was removed under vacuum. The green product was dissolved in 10 mL

of CH_2Cl_2 and precipitated with *n*-hexane, the solution was filtered, and the yellow precipitate was washed twice with 10 mL of *n*-hexane. The yellow powder was dried under vacuum. Yield: 0.2853 g (51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.07 (m, PPh_3), 4.48 (s, 10 H, C_5H_5), 3.77 (s, 8 H, $CNCH_2$), 2.08 (s, 4 H, NCH_2CH_2N) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.7–133.3 (PPh_3), 83.8 (C_5H_5), 51.0 ($CNCH_2$), 48.1 (NCH_2CH_2N) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 42.2 (*s*, *P*Ph_3), –143 (m, *P*F_6) ppm. FT IR (KBr): $\tilde{\nu}$ = 2236 (ν_{CN}), 839 and 522 cm^{-1}(ν_{PF_6}). TOF MS (ES$^+$): *m*/*z* (%) = 691 (100) [RuCp(PPh_3)$_2$]$^+$, 855 (60) [RuCp(PPh_3)$_2$(**1**)]$^+$, 1691 (10) **[M]$^+$**. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 351 (0.8×10^4). Λ_M = 157 $\Omega^{-1}cm^2mol^{-1}$.

Synthesis of 6: [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] (**4**; 0.3667 g, 0.505 mmol) and the ligand *N*,*N*′-bis[*N*′′,*N*′′′-bis(cyanoethyl)aminoethyl]piperazine (**2**; 0.047 g, 0.120 mmol) were introduced with MeOH (45 mL), under nitrogen, into a flame-dried Schlenk flask. $TlPF_6$ (0.2024 g, 0.579 mmol) was added and, after refluxing for 5 h, the mixture was stirred at room temperature for 16 h. The solvent was removed under vacuum and the product was extracted with CH_2Cl_2. After filtration the solvent was removed and the solid was washed twice with diethyl ether. The product was dissolved in 10 mL of CH_2Cl_2 and precipitated with diethyl ether. The yellow powder was dried under vacuum. Yield: 0.1933 g (45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–7.05 (m, PPh_3), 4.47 (s, 20 H, C_5H_5), 2.55 (s, 4 H, NCH_2CH_2N), 2.43 (s, 8 H, $NCCH_2CH_2$) 2.35 (s, 16 H, NCH_2) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 135.7–127.1 (PPh_3), 83.5 (C_5H_5), 55.4 (NCH_2CH_2N piperazine center), 53.1 (inner NCH_2CH_2), 52.3 (inner NCH_2CH_2), 43.5 (outer NCH_2CH_2), 17.9 (CH_2CN) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 42.4 (s, *P*Ph_3), –143 (m, *P*F_6) ppm. FT IR (KBr): $\tilde{\nu}$ = 2259 (ν_{CN}), 840 and 521 cm^{-1}(ν_{PF_6}). TOF MS (ES$^+$): *m*/*z* (%) = 691 (100) [RuCp(PPh_3)$_2$]$^+$, 813 (20) [RuCpPPh_3(**2**)]$^+$, 1075 (25) [RuCp(PPh_3)$_2$(**2**)]$^+$, 1649 (15) [Cp(PPh_3)$_2$CpRu(**2**)RuCpPPh_3][PF_6], 1911 (20) [{RuCp(PPh_3)$_2$}$_2$(**2**)][PF_6], 2746 (60) [{RuCp(PPh_3)$_2$}$_3$(**2**)][PF_6]$_2$, 3583 (10) [M]$^+$. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 350 (1.1×10^4). Λ_M = 279 $\Omega^{-1}cm^2mol^{-1}$.

Synthesis of 7: [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] (**4**; 0.2505 g, 0.345 mmol) and the ligand *N*,*N*,*N*′,*N*′-tetrakis(cyanoethyl)ethylenediamine (**3**; 0.0245 g, 0.177 mmol) were introduced with MeOH (35 mL), under nitrogen, into a flame-dried Schlenk flask. $TlPF_6$ (0.1482 g, 0.424 mmol) was added and, after refluxing for 12 h, the mixture was stirred at room temperature for 12 h. The solvent was removed under vacuum and the product was extracted with CH_2Cl_2. After filtration the solvent was removed and the solid was washed twice with diethyl ether. The product was dissolved in 10 mL of CH_2Cl_2 and precipitated with diethyl ether. The yellow powder was dried under vacuum. Yield: 0.1804 g (60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.06 (m, PPh_3), 4.47 (s, 20 H, C_5H_5), 2.57 (s, 8 H, $NCCH_2CH_2N$), 2.47 (s, 8 H, $NCCH_2$), 2.31 [s, 4 H, $N(CH_2)_2N$] ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 136.1–128.6 (PPh_3), 83.8 (C_5H_5), 52.4 [$N(CH_2)_2N$], 49.0 (NCH_2CH_2CN), 18.9 (CH_2CN) ppm. ^{31}P NMR(202 MHz, $CDCl_3$): δ = 42.5 (s, *P*Ph_3), –143 (m, *P*F_6) ppm. FT IR (KBr): $\tilde{\nu}$ = 2264 (ν_{CN}), 840 and 521 cm^{-1}(ν_{PF_6}). TOF MS (ES$^+$): *m*/*z* = 691 (100) [RuCp(PPh_3)$_2$]$^+$, 963 (7) [RuCp(PPh_3)$_2$(**3**)]$^+$, 1799 (20) [{RuCp(PPh_3)$_2$}$_2$(**3**)][PF_6], 2110 (18) [RuCp(PPh_3)$_2$(**3**)(RuCpPPh_3)$_2$][PF_6]$_2$, 2372 (75) [{RuCp(PPh_3)$_2$}$_2$-(**3**)RuCpPPh_3][PF_6]$_2$, 2634 (70) [{RuCp(PPh_3)$_2$}$_3$(**3**)][PF_6]$_2$, 3471 (18) [M$^+$]. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 351 (0.7×10^4). Λ_M = 313 $\Omega^{-1}cm^2mol^{-1}$.

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