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Article

Synthesis and Reactivity of Poly(propyleneimine) Dendrimers Functionalized with Cyclopentadienone *N*-Heterocyclic-Carbene Ruthenium(0) Complexes

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Abstract: Ligand design in metal chemistry is a fundamental step when pursuing compounds with specific reactivity. In this paper, the functionalization of the OH group in the lateral chain of the *N*-heterocyclic-carbene (NHC) ligand bound to a *bis*-carbonyl cyclopentadienone NHC ruthenium(0) complex allowed the decoration of five generations of poly(propyleneimine) (PPIs) dendrimers with up to 64 organometallic moieties. The coupling was achieved by employing carbonyldiimidazole and the formation of carbamate linkages between dendritic peripheral NH₂ and lateral OH groups on ruthenium complexes. The synthetic procedure, chemical purification, and spectroscopic characterization of the five generations of dendrimers (**3g1–5**) are here described. The ruthenium-modified dendrimers were activated as catalysts in the transfer hydrogenation of the model compound 4-fluoroacetophenone in the presence of cerium ammonium nitrate as their mononuclear congeners. The catalytic activity, being similar for the five generations, shows a decrease if compared to mononuclear complexes. This detrimental effect might be ascribed to the –CH₂NH–functionalization, largely present in dendrimer skeleton and that can compete with the hydrogen transfer mechanism, but also partially to a dendritic effect caused by steric encumbrance.

Keywords: ruthenium; *N*-heterocyclic carbene; ligand functionalization; dendrimers; hydrogen transfer

1. Introduction

Dendritic catalysts are functional macromolecules with precise and unambiguous structures, which, thanks to their monodisperse nature, maintain the advantages of homogeneous catalysts showing fast kinetic responses and easy tunability [1–12]. Furthermore, they can be removed from the reaction mixture by membrane or nanofiltration techniques and precipitation, exploiting their bigger sizes compared to products, and this confers the advantages of heterogeneous catalysts [13]. Catalytic sites grafted on the periphery of dendrimers can give rise to active, multivalent species that might result in high reaction rates. Several reviews report on the use of dendrimers in catalysis [1–11], but few of them are specifically dedicated to the dendrimer effect [14–16]. The consequences of dendritic effects are known to be like substrate activation and influence the reaction rate and selectivity. On one hand, a dendrimer brings together a large number of catalytically active species in a nanoobject, while, on the

other hand, limitation to the access of substrate molecules can lead to a negative effect, i.e., lowering of reaction rates caused by bulk hindrance.

The majority of the reported dendritic catalysts for hydrogenation contain phosphines since they have proved to be optimal ligands for grafting metal complexes, thanks to their ability to firmly coordinate metal ions and lead to high catalytic performances [17–23]. Both negative [24] and positive [25–27] dendritic effects have been observed when hydrogenation is carried out with increasing sizes of dendrimers. On the contrary, less examples regarding transfer hydrogenation are reported [13,28,29]. Worthy of note is the tetrabranched phosphoranyl-terminated carbosilane ruthenium(II) derivative able to catalyze the transfer hydrogenation of cyclohexanone, where cyclohexadiene or formic acid acts as stoichiometric hydrogen donor species. This first-generation dendrimer, which contains the lowest number of peripheral ruthenium functionalities, namely four, was found to be less active than the mononuclear complex [28]. There are also examples in which the dendritic system is given by the surrounding part of the catalytic center [30,31], as in the case of the “green” application of the fluorinated dendritic chiral mono-*N*-tosylated-1,2-diphenylethylenediamine (FTsDPEN), which was employed in the asymmetric transfer hydrogenation of prochiral ketones in aqueous media catalyzed by ruthenium(II) centers [32].

Within the field of transfer hydrogenation, our group has recently developed novel ruthenium compounds for bifunctional catalysis [33,34] by combining cyclopentadienones, which cooperate with the metal centers in catalytic redox reactions [35–38], and *N*-heterocyclic carbenes (NHCs) [39,40], largely used and very versatile ligands due to their easy preparation and the tunability of their steric and electronic properties [41–44]. In particular, the reduction of the model compound 4-fluoroacetophenone catalyzed by complexes **1a–c** (Figure 1) can be activated by addition of cerium ammonium nitrate (CAN), which favors the release of CO [34].

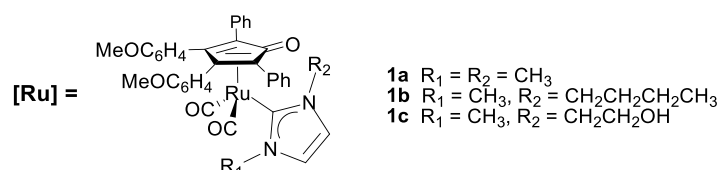
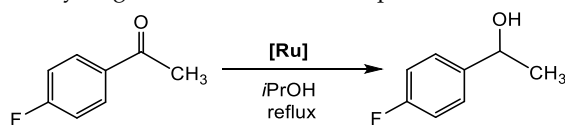


Figure 1. Cyclopentadienone NHC ruthenium(0) complexes **1a–c**.

NHCs are effective tools for the rational design of transition metal catalysts [45–52] in that their skeleton can be provided with suitable substituents for heterogenization (e.g., –OH in **1c**, Figure 1). Despite the fact that NHCs can be considered ancillary ligands as outstanding as phosphines, examples of NHC-decorated dendrimers reported in the literature are still contained [53–56]. These include the NHC-rhodium dendrimer showing a positive dendrimer effect in hydrosilylation of ketones [54], and an NHC-ruthenium derivative employed in olefin metathesis, in which the catalytic center is bonded to the dendrimer through a Ru=C double bond involving the aromatic moiety without exploiting the ancillary NHC ligand [53]. In order to evaluate a possible dendrimer effect and inspired by previous works on dendritic systems [57], we report here on the development of an efficient method for the straightforward synthesis, chemical purification, and spectroscopic characterization of five generations of poly(propyleneimine) (PPIs) NHC-ruthenium(0) functionalized dendrimers with up to 64 organometallic moieties. Their catalytic activity in transfer hydrogenation has been tested for the reduction of 4-fluoroacetophenone in *i*PrOH, and the results obtained will be compared with the ones previously obtained for the mononuclear ruthenium complexes (Table 1) [34].

Table 1. Catalytic transfer hydrogenation of 4-fluoroacetophenone with ruthenium catalysts [Ru].¹

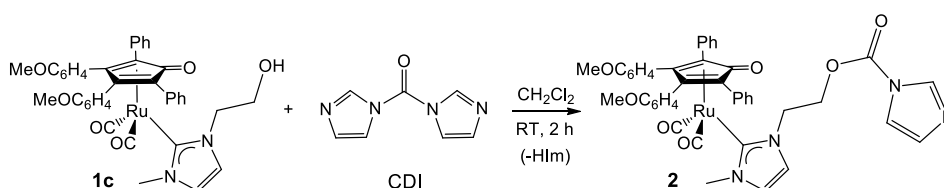
Entry	[Ru]	Additive	Conversion (%) 8 h	Conversion (%) 24 h
1	1a	CAN	25	61
2	1b	CAN	10	87
3	1c	CAN	10	25

¹ General condition: ruthenium complex [Ru] (5 mol %), *i*PrOH (3 mL), reflux (82 °C); conversions were determined by ¹⁹F NMR spectroscopy; 1 mol eq. of CAN per ruthenium center was added.

2. Results

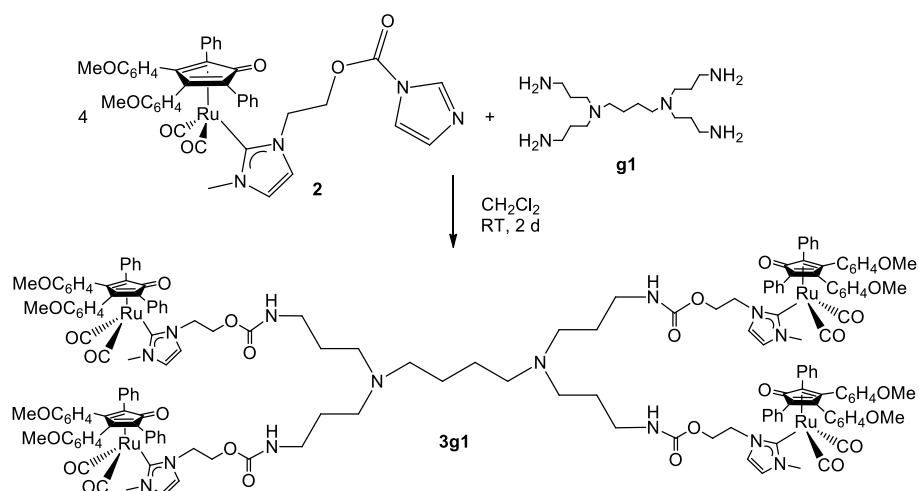
2.1. Synthesis and Characterization of the Ruthenium-Decorated Dendrimers

The new ruthenium(0) complex **2** with CO₂-imidazole (CO₂Im) functionalized NHC ligand was prepared in 84% yield by reacting **1c** with a slight excess of carbonyldiimidazole (CDI: **1c** = 1.1:1) in CH₂Cl₂ at room temperature for 2 h, as shown in Scheme 1. The compound **2** was then easily purified by washing the imidazolium co-product with water.

**Scheme 1.** Synthesis of the ruthenium(0) complex **2** with CO₂Im-functionalized NHC ligand.

The off-white solid **2** is air stable and was characterized by analytical measurements (Figures S1–S4 in the Supplementary Materials, SM). The ¹H and ¹³C NMR spectra were registered in CDCl₃ and they are comparable to the ones of the initial complex **1c** for the unaltered structural parts [34]. In particular, the downfield-shifted resonance of the coordinated carbon atom of the carbene ($\delta = 174.80$ ppm) appeared in the ¹³C NMR spectrum. In addition, the imidazole moiety displays signals at chemical shifts (¹H NMR: $\delta = 8.03, 7.33, 7.08$ ppm; ¹³C NMR: $\delta = 136.95, 130.88, 116.97$ ppm) close to those of the starting material CDI, while the C=O group resonates at 147.89 ppm, typical for a carbamate moiety (–OC(O)N–). In the infrared spectrum in CH₂Cl₂, CO stretching bands ($\nu_{\text{CO}} = 2007$ and 1948 cm^{–1}) are consistent with those of **1c**, and the stretching at 1768 cm^{–1} is ascribable to the carbamate group formed during the reaction. Further evidences of the occurred functionalization reaction were given by Electron-Spray Ionization mass spectrometry (MS-ESI) measurements, where the protonated molecular ion [M + H]⁺ at m/z 823 could be detected.

The reaction in CH₂Cl₂ at room temperature for 2 h of a 4.8 fold excess of **2** with the dendrimer DAB-dendr-(NH₂)₄ (**g1**) led to the formation of the dendrimer **3g1** decorated with four ruthenium(0) moieties (Scheme 2). The CO₂Im group of **2** easily reacted with DAB-dendr-(NH₂)_{*n*} ($n = 8, 16, 32, 64$, **gn**, see Scheme S1 in the SM), up to the fifth generation, under the same experimental conditions yielding the fully functionalized new dendritic organometallic dendrimers **3gn** (Figure 2) in acceptable yields. The excess of **2** and the side products could be easily removed from the crude product by extraction with water and washing with Et₂O. All five generation macromolecules **3gn** were isolated as light brown solids and were revealed to be stable to air and moisture.



Scheme 2. Synthesis of the ruthenium-functionalized first-generation poly(propyleneimine) (PPI) dendrimer **3g1**.

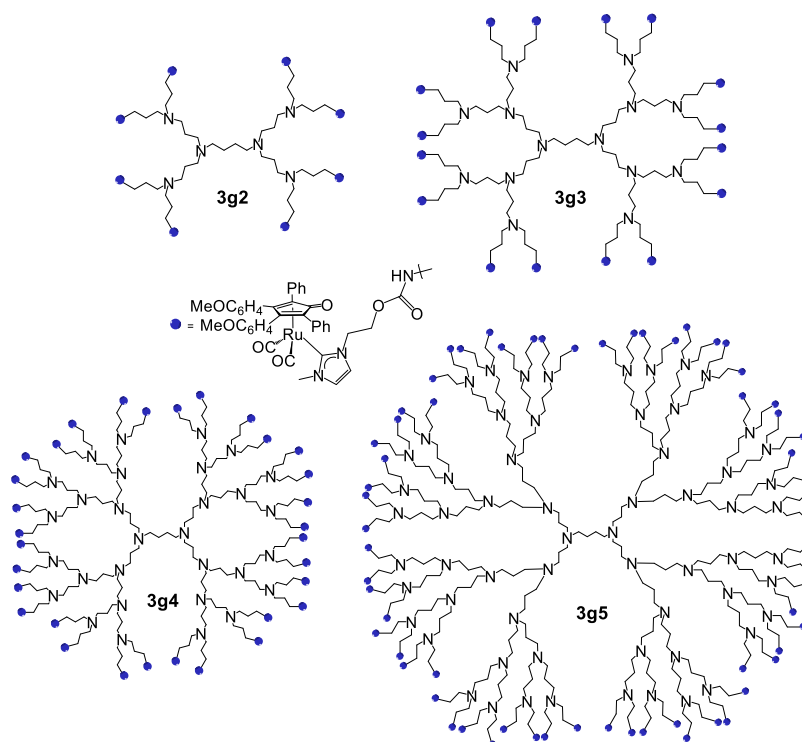


Figure 2. Structure of the second-to-fifth generation dendrimers functionalized with n ruthenium(0) complexes: **3g2** ($n = 8$), **3g3** ($n = 16$), **3g4** ($n = 32$) and **3g5** ($n = 64$).

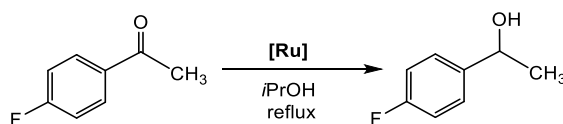
The dendritic compounds are soluble in THF and CH_2Cl_2 , sparingly soluble in Et_2O , and totally insoluble in hexane, toluene as well as aqueous solvents. They were characterized by ^1H and ^{13}C NMR, IR spectroscopy and mass spectrometry, when feasible (Figures S5–S21 in the SM). Considering the NMR spectra registered in CDCl_3 , they show the signals due to the diaminobutane-based PPIs skeleton (^1H : four broad multiplets in the range 3.8–1.3 ppm; ^{13}C : four resonances in the range 63–25 ppm) and those given by the anchored peripheral NHC ruthenium moieties (see Materials and Methods section). Even if all the proton signals appear as broad peaks typical of a polymer-like structure, it is clearly detectable that the resonances of the two methylene groups belonging to the $-\text{NHCCH}_2\text{CH}_2\text{OC}(\text{O})\text{NH}-$ unit of the organometallic moieties are at 3.77 and 3.59 ppm, which are more shielded than those of **2** (4.05 and 3.99 ppm in $-\text{NHCCH}_2\text{CH}_2\text{OC}(\text{O})\text{Im}$). The signal of the NH proton of the carbamate

linkers close to the surface of the PPIs dendrimer moves along the whole spectrum and it is often not clearly detected due to either that it can resonate in the same region of aromatic signals or that it could be engaged in hydrogen bonds like $-\text{NH}\cdots(\text{O})\text{CO}-$ or $-\text{NH}\cdots\text{cyclopentadienone}$, fact that becomes more relevant upon increasing the dendritic generation where the interacting groups get in closer contact. The IR spectra of all five dendritic species in CH_2Cl_2 solution show a strong absorption at 1718 cm^{-1} attributable to both $\text{C}=\text{O}$ and $-\text{O}_2\text{CNH}-$ stretching bands. The structure of the first generation dendrimer **3g1** (Scheme 2) could be also confirmed by MS-ESI, which shows the molecular ion with sodium $[\text{M} + \text{Na}]^+$ at m/z 3355. The high molecular weights of the upper generations **3g2–5** prevented the use of MS-ESI technique for mass detection.

2.2. Catalytic Transfer Hydrogenation

The five generations of functionalized dendrimers **3g1–5** were tested as precursors under catalytic transfer hydrogenation conditions employing 4-fluoroacetophenone as model substrate in refluxing *i*PrOH (hydrogen source). Catalytic runs were performed in order to investigate the stability of the peripheral organometallic moieties on the PPIs dendrimers and to detect any possible dendritic effect. Results obtained are reported in Table 2, and in all cases, selectivity is complete and conversion corresponds to yield.

Table 2. Catalytic transfer hydrogenation of 4-fluoroacetophenone with ruthenium dendrimers **3g1–5** as catalyst **[Ru]**.¹



Entry	[Ru]	Additive	Conversion (%) 8 h	Conversion (%) 24 h
1	3g1	CAN ²	9	17
2	3g2	CAN ²	9	17
3	3g3	CAN ²	7	15
4	3g4	CAN ²	4	15
5	3g5	CAN ²	6	16
6	3g1	pyridine ³	0	20

¹ General conditions: ruthenium complex **[Ru]** (5 mol %), *i*PrOH (3 mL), reflux (82 °C); conversions were determined by ¹⁹F NMR spectroscopy; ² 1 mol eq. of CAN per ruthenium center; ³ 10 mol eq. of pyridine per ruthenium center.

3g1–5 did not show any catalytic activity in the absence of additives, as already observed in the case of the mononuclear congeners [34]. Addition of 1 equivalent of CAN, with respect to Ru loading, promotes CO release [34,35] and leads to the pre-catalyst activation [58] resulting in some catalytic activity. Nevertheless, only 15–17% conversion could be reached after 24 h for all the five generations, which allow us to discard any positive dendritic effect. These conversions are lower than those obtained with the mononuclear alkyl-substituted NHC complexes **1a** and **1b** but similar to **1c** (see Table 1). This peculiar behavior could be then ascribed to $-\text{CH}_2\text{NH}-$ dendrimer functionalization, which might compete with the hydrogen transfer mechanism as indeed depicted previously for the $-\text{CH}_2\text{OH}$ group in **1c** [34].

A similar outcome was found by adding 10 eq. of pyridine for each ruthenium(0) center to **3g1** (entry 6 of Table 2), confirming the activation effect of the latter additive stated for pyridyl functionalized NHC ligands [58]. Although the pre-catalyst activation could be achieved also by pyridine, this was not used to test the following generations of dendrimer due to the high amount of additive required compared to CAN and the limited enhancement in the conversion (20% vs 17%).

3. Materials and Methods

3.1. General Information

Solvents dichloromethane (CH₂Cl₂), diethyl ether (Et₂O), acetonitrile (CH₃CN) and toluene were dried and distilled prior to use. Acetone was degassed and stored under inert atmosphere on molecular sieves. The other solvents *i*PrOH, heptane, hexane, CDCl₃, D₂O and toluene-*d*₈ (Sigma Aldrich) were employed without further purification. DAB-*dendr*-(NH₂)_{*n*} **g1–5** (*n* = 4, 8, 16, 32 and 64), 4-fluoroacetophenone, CDI and CAN (Merck KGaA, Darmstadt, Germany; Sigma-Aldrich Products sold through Sigma-Aldrich, Italy) were employed as purchased. **1c** [39] was prepared as previously reported. The NMR spectra were recorded using Varian Inova 300 (Palo Alto, California - US) (¹H: 300.1 MHz, ¹³C: 75.5 MHz), Varian Mercury Plus VX 400 (Oxford, UK) (¹H: 399.9 MHz; ¹³C: 100.6 MHz, ¹⁹F: 376.5 MHz), Varian Inova 600 (Oxford, UK) (¹H: 599.7 MHz, ¹³C: 150.8 MHz) spectrometers at 298 K; chemical shifts were referenced internally to residual solvent peaks. Full ¹H and ¹³C NMR assignments were done, when necessary, by gHSQC and gHMBC NMR experiments using standard Varian pulse sequences. Infrared spectra were recorded at 298 K on a Perkin-Elmer (Llantrisant, UK) Spectrum Two spectrophotometer. MS-ESI⁺ spectra were recorded with Waters (Milford, MA, USA) Micromass ZQ 4000 spectrometer with samples dissolved in MeOH or CH₃CN. Elemental analyses were performed with the Thermo Scientific Flash 2000 with CHNS analyser (Bremen, Germany) instrument.

3.2. Synthesis of Dicarbonyl(η⁴-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) (1-methyl-3-(2-(CO₂Im-ethyl)imidazol-ylidene)ruthenium (**2**))

1c (1.44 g, 1.98 mmol) and CDI (0.97 g, 5.99 mmol) were dissolved in anhydrous CH₂Cl₂ under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 2 h. The solution was then extracted with water (3 × 20 mL), and traces of water were removed from organic phase with Na₂SO₄. The solvent was then removed under reduced pressure and the white/brown product, identified as **2**, was obtained with an 84% yield. ¹H NMR (399.9 MHz, 298 K, CDCl₃): δ 8.03 (s, 1H, Im); 7.78 (m, 4H, CH_{aryl}), 7.33 (m, 1H, Im), 7.16–7.12 (m, 8H, CH_{aryl}), 7.08 (m, 1H, Im), 7.06 (m, 2H, CH_{aryl}), 6.96 (d, *J* = 2.0 Hz, 1H, CH_{NHC}), 6.85 (d, *J* = 2.0 Hz, 1H, CH_{NHC}), 6.65 (m, 4H, CH_{aryl}), 4.05 (m, 2H, –CH₂–), 3.99 (m, 2H, –CH₂–), 3.72 (s, 6H, –OCH₃), 3.14 (s, 3H, –NCH₃) ppm. ¹³C NMR (100.6 MHz, 298 K, CDCl₃): δ 202.15 (CO), 174.80 (C_{carbene}), 169.41 (C=O, Cp), 158.64 (–COCH₃), 147.89 (–OC(O)N–), 136.95 (CH, Im), 134.91 (C_{qaryl}), 133.55 (CH_{aryl}), 130.88 (CH, Im), 129.36 (CH_{aryl}), 127.63 (CH_{aryl}), 125.63 (C_{qaryl}), 124.70 (CH_{NHC}), 124.37 (CH_{aryl}), 121.76 (CH_{NHC}), 116.97 (CH, Im), 112.96 (CH_{aryl}), 104.09 (C_{2,5}, Cp), 78.88 (C_{3,4}, Cp), 67.02 (–CH₂–), 55.00 (–OCH₃), 49.20 (–CH₂–), 38.41 (CH₃, NHC). IR (CH₂Cl₂): ν(carbonyl CO): 2007 and 1948, ν(C=O, –O₂CIm): 1768 cm^{–1}. MS-ESI⁺ (MeOH): *m/z* 823 [M + H]⁺, 845 [M + Na]⁺. Anal. Calcd (%) for C₄₃H₃₆N₄O₇Ru: C, 62, 84; H, 4, 42; N, 6, 82. Found: C, 62, 81; H, 4, 43; N, 6, 83. ¹H and ¹³C NMR, IR and MS-ESI spectra of **2** are reported in Figures S1–S4 in the SM.

3.3. Synthesis of Functionalized Dendrimers **3g1–5**

g1 (0.021 g, 0.06 mmol) and **2** (0.260 g, 0.31 mmol) were dissolved in anhydrous CH₂Cl₂ (10 mL) under inert atmosphere and the reaction mixture was stirred at room temperature for two days. The solution was then extracted with water (3 × 20 mL) and traces of water were removed from organic phase with MgSO₄. Organic solvent was removed under reduced pressure and the solid crude was washed with Et₂O (3 × 15 mL). The final yellow solid was identified as **3g1** (*n* = 4) and obtained with 42% yield. ¹H NMR (399.9 MHz, 298 K, CDCl₃): δ 7.72–6.60 (CH_{aryl}), 6.81 (m, 4H, CH_{NHC}), 6.62 (m, 4H, CH_{NHC}), 3.77 (m, 8H, –CH₂–), 3.68 (s, 24H, –OCH₃), 3.59 (m, 8H, –CH₂–), 3.09 (s, 12H, –NCH₃), 3.07, 2.97, 2.36, 1.57, 1.36 (br, 32H, CH₂, DAB-*dendr*) ppm. ¹³C NMR (100.6 MHz, 298 K, CDCl₃): δ 202.06 (C=O), 172.67 (C_{carbene}), 169.56 (C=O, Cp), 158.53 (–COCH₃), 156.00 (–OC(O)N–), 135.04 (C_{qaryl}), 133.55 (CH_{aryl}), 129.40 (CH_{aryl}), 127.45 (CH_{aryl}), 125.50 (C_{qaryl}), 124.44 (CH_{aryl}), 124.36 (CH_{NHC}), 121.80 (CH_{NHC}), 112.85 (CH_{aryl}), 103.73 (C_{2,5}, Cp), 78.97 (C_{3,4}, Cp), 63.29 (–CH₂–), 54.96 (–OCH₃), 49.75 (–CH₂–), 38.25 (CH₃, NHC), 53.73, 51.65, 39.51, 26.99, 24.88 (CH₂, DAB-*dendr*) ppm. IR (CH₂Cl₂): ν(carbonyl CO):

2006 and 1947, $\nu(\text{C}=\text{O}, -\text{NHC}(\text{O})\text{O}-)$: 1718, $\nu(\text{C}=\text{C})$: 1601 and 1518, $\nu(\text{C}=\text{O}, \text{Cp})$: 1582 cm^{-1} . MS-ESI⁺ (CH_3CN): m/z 3355 $[\text{M} + \text{Na}]^+$. Anal. Calcd (%) for $\text{C}_{176}\text{H}_{168}\text{N}_{14}\text{O}_{28}\text{Ru}_4$: C, 63, 45; H, 5, 08; N, 5, 89. Found: C, 63, 46; H, 5, 08; N, 5, 88. ¹H and ¹³C NMR, IR and MS-ESI spectra of **3g1** are reported in Figures S5–S9 in the SM.

The upper generations of dendrimers, peripherally decorated with n ruthenium(0) moieties, **3g2–5** with $n = 8, 16, 32$ and 64 , respectively, were prepared by applying the same procedure, but they required seven days of reaction time. ¹H and ¹³C NMR spectra are reported in Figures S10–S21 in the SM.

3g2, prepared from **g2** (0.020 g, 0.03 mmol) and **2** (0.26 g, 0.31 mmol), yield of 25%. ¹H NMR (399.9 MHz, 298 K, CDCl_3): δ 7.75–6.61 (CH_{aryl}), 6.96 (m, 8H, CH_{NHC}), 6.79 (m, 8H, CH_{NHC}), 3.77 (m, 16H, $-\text{CH}_2-$), 3.70 (s, 48H, $-\text{OCH}_3$), 3.59 (m, 16H, $-\text{CH}_2-$), 3.10 (s, 24H, $-\text{NCH}_3$), 3.20–2.80, 2.60–2.20, 1.96–1.42 (br, 80H, CH_2 , DAB-dendr) ppm. ¹³C NMR (100.6 MHz, 298 K, CDCl_3): δ 202.18 (C=O), 173.96 ($\text{C}_{\text{carbene}}$), 169.52 (C=O, Cp), 158.61 ($-\text{COCH}_3$), 156.14 ($-\text{OC}(\text{O})\text{N}-$), 135.00 (C_{qaryl}), 133.58 (CH_{aryl}), 129.49 (CH_{aryl}), 127.59 (CH_{aryl}), 125.78 (C_{qaryl}), 124.55 (CH_{aryl}), 124.30 (CH_{NHC}), 122.43 (CH_{NHC}), 112.95 (CH_{aryl}), 103.65 (C2,5, Cp), 78.68 (C3,4, Cp), 63.29 ($-\text{CH}_2-$), 55.02 ($-\text{OCH}_3$), 50.00 ($-\text{CH}_2-$), 38.31 (CH_3 , NHC), 53.47, 51.54, 39.51, 26.84, 23.63 (CH_2 , DAB-dendr) ppm. IR (CH_2Cl_2): $\nu(\text{carbonyl CO})$: 2008 and 1948; $\nu(\text{C}=\text{O}, -\text{NHC}(\text{O})\text{O}-)$: 1719; $\nu(\text{C}=\text{C})$: 1603 and 1518; $\nu(\text{C}=\text{O}, \text{Cp})$: 1577 cm^{-1} . Anal. Calcd (%) for $\text{C}_{360}\text{H}_{352}\text{N}_{30}\text{O}_{56}\text{Ru}_8$: C, 63, 55; H, 5, 21; N, 6, 18. Found: C, 63, 54; H, 5, 19; N, 6, 19.

3g3, prepared from **g3** (0.021 g, 0.01 mmol) and **3** (0.17 g, 0.21 mmol), yield of 32%. ¹H NMR (399.9 MHz, 298 K, CDCl_3): δ 7.76–6.61 (CH_{aryl}), 6.96 (m, 16H, CH_{NHC}), 6.78 (m, 16H, CH_{NHC}), 3.77 (m, 32H, $-\text{CH}_2-$), 3.71 (s, 96H, $-\text{OCH}_3$), 3.67 (m, 32H, $-\text{CH}_2-$), 3.10 (s, 48H, $-\text{NCH}_3$), 3.20–1.50 (br, 176H, CH_2 , DAB-dendr) ppm. ¹³C NMR (100.6 MHz, 298 K, CDCl_3): δ 202.17 (C=O), 173.94 ($\text{C}_{\text{carbene}}$), 169.46 (C=O, Cp), 158.60 ($-\text{COCH}_3$), 153.57 ($-\text{OC}(\text{O})\text{N}-$), 135.00 (C_{qaryl}), 133.57 (CH_{aryl}), 129.29 (CH_{aryl}), 127.59 (CH_{aryl}), 125.52 (C_{qaryl}), 124.54 (CH_{aryl}), 124.29 (CH_{NHC}), 122.38 (CH_{NHC}), 112.95 (CH_{aryl}), 103.98 (C2,5, Cp), 78.67 (C3,4, Cp), 63.69 ($-\text{CH}_2-$), 55.01 ($-\text{OCH}_3$), 50.01 ($-\text{CH}_2-$), 38.30 (CH_3 , NHC), 53.39, 51.39, 38.41, 26.78, 24.02 (CH_2 , DAB-dendr) ppm. IR (CH_2Cl_2): $\nu(\text{carbonyl CO})$: 2008 and 1949, $\nu(\text{C}=\text{O}, -\text{NHC}(\text{O})\text{O}-)$: 1718, $\nu(\text{C}=\text{C})$: 1602 and 1517, $\nu(\text{C}=\text{O}, \text{Cp})$: 1577 cm^{-1} . Anal. Calcd (%) for $\text{C}_{728}\text{H}_{720}\text{N}_{62}\text{O}_{112}\text{Ru}_{16}$: C, 63, 61; H, 5, 28; N, 6, 32. Found: C, 63, 60; H, 5, 30; N, 6, 33.

3g4, prepared from **g4** (0.020 g, 6.00 μmol) and **3** (0.20 g, 0.25 mmol), yield of 41%. ¹H NMR (399.9 MHz, 298 K, CDCl_3): δ 7.75–6.60 (CH_{aryl}), 6.96 (m, 32H, CH_{NHC}), 6.79 (m, 32H, CH_{NHC}), 3.77 (m, 64H, $-\text{CH}_2-$), 3.71 (s, 192H, $-\text{OCH}_3$), 3.67 (m, 64H, $-\text{CH}_2-$), 3.10 (s, 96H, $-\text{NCH}_3$), 3.20–1.50 (br, 368H, CH_2 , DAB-dendr) ppm. ¹³C NMR (100.6 MHz, 298 K, CDCl_3): δ 202.16 (C=O), 173.88 ($\text{C}_{\text{carbene}}$), 169.38 (C=O, Cp), 158.60 ($-\text{COCH}_3$), 153.58 ($-\text{OC}(\text{O})\text{N}-$), 134.97 (C_{qaryl}), 133.57 (CH_{aryl}), 129.31 (CH_{aryl}), 127.59 (CH_{aryl}), 125.54 (C_{qaryl}), 124.53 (CH_{aryl}), 124.30 (CH_{NHC}), 122.38 (CH_{NHC}), 112.95 (CH_{aryl}), 103.96 (C2,5, Cp), 78.75 (C3,4, Cp), 63.68 ($-\text{CH}_2-$), 55.02 ($-\text{OCH}_3$), 49.99 ($-\text{CH}_2-$), 38.32 (CH_3 , NHC), 52.47, 51.22, 38.43, 24.10, 19.73 (CH_2 , DAB-dendr) ppm. IR (CH_2Cl_2): $\nu(\text{carbonyl CO})$: 2009 and 1947, $\nu(\text{C}=\text{O}, -\text{NHC}(\text{O})\text{O}-)$: 1718, $\nu(\text{C}=\text{C})$: 1603 and 1518, $\nu(\text{C}=\text{O}, \text{Cp})$: 1576 cm^{-1} . Anal. Calcd (%) for $\text{C}_{1464}\text{H}_{1456}\text{N}_{126}\text{O}_{224}\text{Ru}_{32}$: C, 63, 63; H, 5, 31; N, 6, 39. Found: C, 63, 61; H, 5, 31; N, 6, 39.

3g5, prepared from **g5** (0.021 g, 3.00 μmol) and **3** (0.20 g, 0.25 mmol), yield of 43%. ¹H NMR (399.9 MHz, 298 K, CDCl_3): δ 7.75–6.58 (CH_{aryl}), 6.96 (m, 64H, CH_{NHC}), 6.78 (m, 64H, CH_{NHC}), 3.77 (m, 128H, $-\text{CH}_2-$), 3.71 (s, 384H, $-\text{OCH}_3$), 3.66 (m, 128H, $-\text{CH}_2-$), 3.10 (s, 192H, $-\text{NCH}_3$), 3.20–1.50 (br, 752H, CH_2 , DAB-dendr). ¹³C NMR (100.6 MHz, 298 K, CDCl_3): δ 202.16 (C=O), 173.91 ($\text{C}_{\text{carbene}}$), 169.43 (C=O, Cp), 158.60 ($-\text{COCH}_3$), 153.57 ($-\text{OC}(\text{O})\text{N}-$), 134.98 (C_{qaryl}), 133.57 (CH_{aryl}), 129.30 (CH_{aryl}), 127.59 (CH_{aryl}), 125.53 (C_{qaryl}), 124.54 (CH_{aryl}), 124.30 (CH_{NHC}), 122.38 (CH_{NHC}), 112.95 (CH_{aryl}), 103.97 (C2,5, Cp), 78.70 (C3,4, Cp), 63.80 ($-\text{CH}_2-$), 55.02 ($-\text{OCH}_3$), 49.92 ($-\text{CH}_2-$), 38.31 (CH_3 , NHC), 52.46, 51.35, 38.39, 26.70, 24.09 (CH_2 , DAB-dendr). IR (CH_2Cl_2): $\nu(\text{carbonyl CO})$: 2006 and 1950, $\nu(\text{C}=\text{O}, -\text{NHC}(\text{O})\text{O}-)$: 1717, $\nu(\text{C}=\text{C})$: 1602 and 1518, $\nu(\text{C}=\text{O}, \text{Cp})$: 1577 cm^{-1} . Anal. Calcd (%) for $\text{C}_{2936}\text{H}_{2928}\text{N}_{254}\text{O}_{448}\text{Ru}_{64}$: C, 63, 64; H, 5, 33; N, 6, 42. Found: C, 63, 64; H, 5, 35; N, 6, 41.

3.4. General Procedure for Transfer Hydrogenation

Functionalized dendrimer (5 mol % [Ru]), CAN (1 eq.) or pyridine (10 eq.) and *i*PrOH (3 mL) were stirred at reflux for 15 min. Then 4-fluoroacetophenone (36 μ L, 300 μ mol) was added and sampling was done at regular intervals by withdrawing aliquots (about 0.05 mL) of the reaction mixture and diluting them with addition of CDCl₃ (0.5 mL). Conversions were determined by ¹⁹F NMR spectroscopy by monitoring signals at $\delta = -105.35$ (4-fluoroacetophenone) and -115.70 ppm (1-(4-fluorophenyl)ethanol). Further details are given in Figures S22–S23 and Tables S1–S2 in the SM.

4. Conclusions

Five generations of novel cyclopentadienone-NHC-ruthenium(0)-functionalized PPIs dendrimers **3g1–5** with up to 64 organometallic peripheral moieties have been here successfully prepared and provide a precious route for the immobilization of hydroxy-functionalized NHC complexes onto organic and inorganic amino-decorated supports. The dendrimers **3g1–5** also represent one of the few examples in which NHC ligands are exploited as ancillary ligands for the functionalization of high-generation dendrimers. The stability shown by these dendrimers highlights a significant opportunity to obtain nanosized multinuclear systems, which have the potential to work in between homogeneous and heterogeneous catalytic regimes.

Dendrimers **3g1–5**, thanks to the ruthenium(0) centers present at the periphery, are active in the transfer hydrogenation of 4-fluoroacetophenone in the presence of additives like CAN or pyridine. In line with what previously observed for the corresponding mononuclear species **1c**, the limited catalytic activity is more likely due to dendrimer $-\text{CH}_2\text{NH}-$ functionalization rather than ascribable to a sterically induced detrimental dendrimer effect. Nevertheless, taking advantage of the synthetic strategy here described, further studies will be devoted in the future to improve the catalytic activity, for example by modifying the dendritic linker.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/2/264/s1>, Scheme S1: Poly(propyleneimine) (PPIs) dendrimers used as support for ruthenium complexes in this work; Figures S1–S4: ¹H and ¹³C NMR, IR and MS-ESI spectra of **2**; Figures S5–S21: ¹H and ¹³C NMR, IR and MS-ESI spectra of **3g1–5**; Figures S22 and S23: ¹⁹F NMR spectra for catalytic transfer hydrogenation of 4-fluoroacetophenone with **3g1–5**; Tables S1 and S2: ¹⁹F NMR conversion data for catalytic transfer hydrogenation of 4-fluoroacetophenone with **3g1–5**.

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