Giant Cobalticinium Dendrimers

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Giant redox dendrimers were synthesized with pentamethylcobalticinium termini for the fifth, sixth, and seventh generations (in addition to the nine-arm generation 0) up to a theoretical number of 3⁹ tethers (seventh generation, G₇). Therefore, a functional pentamethyl cobalticinium derivative was synthesized with a long arm. This tether-lengthening strategy was used as in the previously reported ferrocenyl and pentamethylferrocenyl series to overcome the bulk constraint at the periphery of short-tethered dendrimers. These polycationic cobalt-sandwich metallodendrimers were characterized by ¹H, ¹³C, and ²⁹Si NMR, MALDI-TOF mass spectrometry (for generation 0), elemental analysis, UV–vis spectroscopy, dynamic light scattering (DLS), atomic force microscopy (AFM), and cyclic voltammetry. UV–vis spectroscopy and analytical data are consistent with a moderate amount of defects (G₅ and G₆) that largely increases for G₇ (which contains 14 000 ± 1000 pentamethylcobalticinium termini). Cyclic voltammetry reveals full chemical and electrochemical reversibility for the cathodic reduction [dendr-C₅H₄Co^{III}Cp*]⁺ \rightarrow [dendr-C₅H₄Co^{III}Cp*] up to G₇ as in the iron-sandwich series, showing that electron transfer is fast among the flexible peripheral redox sites.

Introduction

Metallodendrimers¹ belong to the rich family of metalcontaining macromolecules² that have potential applications in material science,³ biology,⁴ and catalysis.⁵ In particular, ferrocenyl dendrimers⁶ have attracted much attention because of their properties in molecular electronics, sensing, redox catalysis, and templates for the fabrication of precise nanoparticles of catalytic interest.⁷

Since their first synthesis by Wilkinson in 1952,⁸ cobalticinium salts (also named cobaltocenium) have been the subject of attention,⁹ because their redox robustness provides a useful electrochemistry and electron-transfer chemistry

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including very stable (although air -sensitive and reactive) neutral cobaltocene,¹⁰ a so-called "19-electron" complex, and a very electron-rich species, the 20-electron cobaltocene anion.¹¹ The cobalticinium moiety has been used *inter alia* to design coordination polymers,¹² organic-organometallic crystals,¹³ and metal-containing polymers,¹⁴ for ion pairing with metal–carbonyl anions,¹⁵ for anion recognition,¹⁶ to induce radical polymerization,¹⁷ and as a starting point to

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build polyolefin and polybenzyl dendritic cores.¹⁸ Although many ferrocenyl dendrimers are known,^{6,7} there are only few reports on cobalticinium dendrimers,^{19,20} and the known cobalticinium dendrimers are relatively small. Recently, we constructed giant ferrocenyl dendrimers based on the tetherlengthening strategy in order to provide more space around the dendrimer periphery so that they can be functionalized with redox groups at the end of the tethers of giant dendrimers.^{7g} Indeed, the de Gennes dense-packing limit,²¹ which applied to Tomalia' seminal giant PAMAM dendrimers,²² predicted a steric limit to the number of generations due to periphery bulk.²¹ Although we have shown that backfolding of small termini toward the dendrimer's center thus

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Scheme 1. Schematic Representation of the Tether-Lengthening Strategy for the Introduction of Bulky Functional Groups at the Periphery of Large Dendrimers



partially circumvent the dense packing limit,^{23,24} back-folding is all the less possible as the termini are larger.²⁵ For instance, with a former dendrimer series for which the tethers were terminated by amidoferrocenyl groups, insolubility was reached for a dendrimer containing 36 redox termini.^{7a} Thus, using the tether-lengthening construction, it was possible to synthesize dendrimers with up to the seventh generation with approximately 14 000 ferrocenyl units.⁹ We now report the use of a related strategy (Scheme 1) to synthesize giant dendrimers terminated by cobalticinium groups. The syntheses, characterizations, and electrochemical properties of the resulting giant pentamethylcobalticinium dendrimers are detailed in this article.

Results and Discussion

The strategy of lengthening the dendrimer tethers was applied by introducing, in the cobalt-sandwich moiety, a presynthesized functional cyclopentadienyl ligand bearing a long chain terminated by an olefinic group. We choose the pentamethylcyclopentadienyl ancillary ligand because of its ability to stabilize the precursor cobalt(III) species, and the robustness and solubility properties that it brings to the cobalt system including its dendritic series. Note the difference of approach compared to the giant dendritic ferrocene series whereby the metallocene was functionalized, due to its rich electrophilic chemistry, before binding to the dendrimers.

1. Synthesis of the Organic Dendrimers. The dendritic construction starts by the known nona-allylation of $[FeCp(\eta^6-mesitylene)][PF_6]^{26}$ giving the nona-allyl organic compound

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1 after decomplexation, using visible light,²⁷ of the dendritic cores. It follows our previously reported procedure for the iterative synthesis of giant polyolefin dendrimers that had been constructed until generation 9 according to a catalytic hydrosilylation/Williamson sequence of reactions (Schemes 2 and 3).²³ In this $1 \rightarrow 3$ connectivity pioneered by Newkome,²⁸ the number of terminal allyl branches is multiplied by

3 from a generation to the next one and is thus equal to 3^{n+2} , the dendritic core of generation 0 containing 3^2 terminal allyl groups.²⁹

2. Functionalization of the Dendrimers with the Pentamethylcobalticinium Termini. The pentamethylcyclopentadienyl-cobalt chloride intermediate resulting from the reaction between cobalt trichloride and pentamethylcyclopen-

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Scheme 4. Synthesis of the Pentamethylcobalticinium Salt 14 Containing a Long Alkyl Chain and a Phenol Termini



tadienyllithium is stable enough, in a dimeric form (unlike the iron analogue), to withstand further substitution of the chloride ligands by a functional cyclopentadienyl group.³⁰ This property allows the direct synthesis at -60 °C in THF of cationic mixed cobalticinium derivatives containing both the pentamethylcy-clopentadienyl and the functional cyclopentadienyl ligands. Thus, the functionalized cyclopentadienyl **10** was used in the synthesis of the pentamethylcobalticinium salt, yielding the functionalized pentamethylcobalticinium salt **11**. Hydrosilylation



of **11** with (dimethyl)chloromethylsilane in the presence of Kartsted catalyst yielded compound **12**. After substitution of chloride by iodide yielding **13**, Williamson reaction with hydroquinone afforded the phenolic derivative **14** (Scheme 4).

The pentamethylcobalticinium dendrimers (Co^{*}) were synthesized using the Williamson reaction between the iodomethyl dendrimers and **14**. The reaction was carried out for G₀, G₅, G₆, and G₇, and these metallodendrimers were characterized by ¹H, ¹³C, and ²⁹Si NMR, elemental analysis, UV/vis spectroscopy, dynamic light scattering, and cyclic voltammetry (eqs 1–4). The dendrimer **15** (G₀-Co^{*}) shows a broad peak near 6500 Da (calcd for [C₃₇₈H₆₀₆O₁₈Si₁₈Co₉]⁹⁺: 6 474.00 Da) in the MALDI-TOF mass spectra. The elemental analyses of **16** (G₅-Co^{*}), **17** (G₆-Co^{*}), and **18** (G₇-Co^{*}) show a carbon deficiency that becomes very important for G₇-Co^{*}, a general trend for giant dendrimers of that generation, attributable to the enormous encapsulation capacity (inorganic salts).

$$\begin{array}{c} \text{G}_{7}\text{-}19683\text{-}\text{CH}_2\text{I} & \underbrace{\mathbf{14}, \text{K}_2\text{CO}_3}_{\text{DME}, 80 \,^\circ\text{C}, 48\text{h}} & \begin{array}{c} \text{G}_7\text{-}19683\text{-}\text{Co}^\circ\text{PF}_6 \\ (\mathbf{18}) & \begin{array}{c} \text{(13)} \end{array} \end{array}$$

3. Characterization of the Metallodendrimers 3.1. UV– Vis Spectroscopy. In order to estimate the number of defects in the dendritic structures due to the divergent synthesis, we investigated the UV–vis spectroscopy of the metallodendrimers. The Lambert–Beer law ($A = \varepsilon lc$) was used to determine the actual total number of metallocene groups in the dendrimers.¹⁸ The UV–vis spectra of the metallocenes present an absorption band at 399 nm in this pentamethylcobalticinium series. The number of metallocene termini in each dendrimer can be estimated by comparing the molar extinction coefficient ε of the dendrimers with that of the corresponding monomer (ε_0). In the ferrocenyl series, the linearity of the absorption with the number of redox groups in the low-generation metallodendrimers confirmed that there is no interaction between the metallocenyl groups that would perturb the validity of the Lambert–Beer

Table 1. Number of Branches Calculated Using the Lambert-Beer Law for Pentamethylcobalticinium Dendrimers

dendrimer	λ (nm)	theoretical number of brances	ε	calculated ^a number of branches
monomer 14	399	1	$\epsilon_0 = 566$	
G ₀ -Co* (15)	399	9	5319	9 ± 1
G ₅ -Co* (16)	399	2187	1 105 973	2000 ± 100
G ₆ -Co* (17)	399	6561	3 603 810	6400 ± 300
G7-C0* (18)	399	19 683	8 122 100	14000 ± 1000

 $^{a}\varepsilon/\varepsilon_{0}$ represents the experimental branch number calculated from the Lambert–Beer law.

law.²³ Thus, we tentatively assume that this same law applies to the cobalticinium dendrimers, although the dendrimers from generations 1 to 4 were not synthesized. The number of termini calculated using the Lambert-Beer law confirms the existence of the defects in the dendritic structures that is marked for the high generations (Table 1). More specifically, these defects are not present in G_0 , they are relatively not numerous for generations 5, but their number increases from G₅ to G₇ and reached a high level for this last generation. The structural defects are present in similar amounts independently of the nature of the peripheral redox group. For example, G₅-Fc (Fc: ferrocenvl), G₅-Fc* (Fc*: pentamethylferrocenvl), and G₅-Co* present an experimental number of termini of 2000 ± 100 , and G7-Fc, G7-Fc*, and G7-Co* all present an experimental number of termini of 14 000 \pm 1000. The similarity of these data for the iron and cobalt series of dendrimers indicates that the defects in the metallodendrimer structures are attributable to the divergent construction rather than to metallocene branching.

3.2. Dynamic Light Scattering (DLS). DLS is a very useful technique for the characterization of the metallodendrimers, because it allows the determination of the size (hydrodynamic diameter) of the dendrimers in solution and consequently their diffusion coefficient (*D*) using the Stokes–Einstein equation $D = kT/6\pi\eta R_{h}$, where the R_{h} is the hydrodynamic radius, η is the solvent viscosity, *k* is the Boltzmann constant, and *T* is the temperature. It is known that dendrimers present globular shapes, and usually they are considered as perfect spheres in order to determine their physical properties. We also used this approximation to calculate the volume and the density of these metallodendrimers (Table 2).

3.3. Cyclic Voltammetry. The four generations of pentamethylcobalticinium dendrimers were studied by cyclic voltammetry. The cyclic voltammograms were recorded using dichloromethane, acetonitrile, or dimethylformamide (DMF) as the solvent. For the first reduction wave that corresponds to the reduction of cobalticinium derivatives to cobaltocenes, in dichloromethane, this wave is single and reversible and, in first approximation (neglecting the electrostatic and statistic factors that are very weak), at the same potential as that of monomeric pentamethyl cobaltocene.^{10,11,18,31–34} The unicity of the first reduction wave is observed in dichloromethane or acetonitrile at -1.16 V vs FeCp₂* (electrolyte: [n-Bu₄N][PF₆] 0.1 M, scan

rate: 200 mV s⁻¹, 20 °C, working and counter electrodes: Pt; quasi-reference electrode: Ag). The adsorption phenomenon is important specifically in acetonitrile, probably due to the low solubility of the reduced neutral dendrimer in acetonitrile (Figure 1). DMF was used in order to observe the second reduction wave Co^{II}/Co^I (Figure 2). In dichloromethane, the calculation of the number of electrons using the Anson–Bard equation³⁵ for G₅-Co* gives a difference of only 20% (number of electrons found is 2628 instead of 2187) attributable to adsorption.

The single wave can be explained by the weakness of the electrostatic factor³⁶ (influence of ion pairing^{36,37}) among the redox sites of the metallodendrimers, these redox centers being very far from one another (large through-bond distances). The electrochemical reversibility observed for all the generations in dichloromethane shows that the electron-hopping mechanism among the redox centers of the periphery is extremely efficient.^{4b,9} Thus, electron transfer is fast between all the redox groups of the dendrimers and the electrode. The electron-hopping mechanism in metallodendrimers has been proposed by Amatore et al.^{38a,b} for dendrimers containing 64 peripheral branches terminated by $[Ru(terpy)_2]^{2+}$. It is based on the measured electronhopping rate constant using ultramicroelectrodes and on a Smoluchowski-type model developed to take into account viscosity effects during the displacement of the Ru^{III}/Ru^{II}(tpy)₂ redox centers around their equilibrium positions.^{38c} These studies involved ultramicroelectrodes with very fast scan rates.³⁹ Accordingly, the events have time to proceed within the time scale of the present studies. Also note that the dendrimers rotate fast within the electrochemical time scale, so that all the redox groups come close to the electrode within this time scale.⁴⁰ Fast rotation alone can explain the fast heterogeneous electron transfer with the small dendrimers. For the high generation, however, the hopping mechanism between nearby centers appears to be much easier than the fast-rotation mechanism. In DMF, the second reduction wave Co^{II}/Co^{I} is observed at -2.19V vs FeCp*2 and looks fairly normal,11 although not fully chemically reversible. On the other hand, the first wave appears considerably flattened, indicating that that all the Co^{III} centers are not reduced at the same potential (same trend for the oxidation of CoII) because of a very substantial electrostatic factor.³⁶ The solvent considerably influences ion pairing, whose energy plays an important role in the redox potential.³⁶ Thus DMF strongly coordinates to the cationic Co^{III} species, unlike the other solvents, which provokes the redox-potential distinction among the redox sites of the dendrimer, and a broad envelope of redox waves is observed. The Co^{II}/Co^I wave¹¹ does not involve cations, and this phenomenon does not appear, which indicates that it is specific to cations.

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 Table 2. Hydrodynamic Diameter of the Pentamethylcobalticinium Dendrimers Obtained by DLS and Calculated Diffusion Coefficient, Volume, and Density of These Metallodendrimers

dendrimer ^a	$\begin{array}{c} MW\\ (g \ mol^{-1}) \end{array}$	hydrodynamic diameter ^b (nm)	diffusion coefficient ^{c} (m ² s ⁻¹)	volume ^d (m ³)	density (kg/m ³)
G ₅ -Co* (16)	2 101 351	28.5 ± 0.7	3.41×10^{-14}	$(1.21 \pm 0.2) \times 10^{-23}$	$(2.9\pm0.1)\times10^2$
G_6 -Co* (17)	6 305 795	30.0 ± 0.8	3.24×10^{-14}	$(1.41 \pm 0.2) \times 10^{-23}$	$(7.4 \pm 0.4) \times 10^2$
G7-C0* (18)	18 919 128	32.1 ± 1.1	3.03×10^{-14}	$(1.73 \pm 0.2) \times 10^{-23}$	$(1.8 \pm 0.2) \times 10^3$

^{*a*} It was not possible to obtain the hydrodynamic diameter of the dendrimer of G₀ by DLS, because its size is below the limit for this technique. ^{*b*} Measured at 25 °C in acetone; the hydrodynamic diameter value was obtained from statistical CONTIN analysis with 2% error. ^{*c*} Calculated using the Stokes–Einstein equation. ^{*d*} Considering the globular dendrimer shape a perfect sphere ($V = (4/3)\pi r^3$).



Figure 1. Cyclic voltammograms obtained for the G₅-Co* (Co^{III}/Co^{II}), in (a) dichloromethane and (b) acetonitrile (3 cycles).



Figure 2. Cyclic voltammograms obtained for the G₆-Co* in DMF. $E_{1/2}(\text{Co}^{II}/\text{Co}^{I}) = -1.19 \text{ V vs FeCp}_2^* \text{ and } E_{1/2}(\text{Co}^{II}/\text{Co}^{I}) = -2.19 \text{ V vs FeCp}_2^*.$

Conclusion

Functional pentamethylcobalticinium hexafluorophosphate salts have been synthesized by successive introduction of the ancillary pentamethylcyclopentadienyl ligand followed by that of the functional cyclopentadienyl ligand onto Co^{III}. The long functional tether of the monosubstituted cyclopentadienyl ligand allowed the synthesis of giant dendrimers containing a theoretical number of 3^{n+2} pentamethylcobalticinium termini, *n* being the generation number. This robust redox group was connected to organic dendrimers using a Williamson coupling reaction between a phenol group located at the termini of the metallocene substituent and the iodomethylsilyl group located at the dendrimer branch termini. The metallodendrimers, synthesized for the generation 0 and 5-7, were shown by UV-vis spectroscopy to contain a number of redox groups that are relatively close to the theoretical ones until G_6 with numbers of defects increasing as the generation number increases. The size increase of the dendrimers from G₅ to G₇ is also clearly observed in the DLS experiments. The last generation, G7, contained a large number of defects, however, as the number of terminal branches, as in the ferrocenyl and pentamethylferrocenyl dendrimer series, was only 14 000 \pm 1000 instead of the theoretical number of 19 683. The full chemical and electrochemical reversibility was maintained in cyclic voltammetry, with CH₂Cl₂ as the solvent, until G₇, confirming a fast electron-hopping mechanism as in the ferrocenyl series in this solvent. On the other hand, in DMF, 

strong DMF-Co^{II} cation interaction differentiates the redox sites by the electrostatic factor within a polycationic metallodendrimer. The analogy of results in the Co and Fe sandwichterminated dendrimers indicates that the tether-lengthening strategy works in both series and that the defects are due to the divergent dendritic organic core construction rather than to functionalization with the redox groups. Finally, these metallodendrimers provide fast electron-transfer connectors, and a behavior of stable molecular batteries is anticipated and will be the subject of further studies (Scheme 5).

Experimental Section

General Data. Solvents, Compounds, and Reactions. Reagentgrade diethyl ether and tetrahydrofuran (THF) were predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. Dichloromethane and acetonitrile were distilled from calcium hydride just before use. All other solvents and chemicals were used as received. Kartsted catalyst and dry DMF were purchased from Aldrich. The organic dendrimers²³ used here and the phenoltriallyl dendronic brick p-HOC₄H₄C(CH₂CH= CH₂)₃⁴¹ were synthesized according to our previous reports.

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NMR Spectroscopy. ¹H NMR spectra were recorded at 25 °C with a Bruker AC 300 (300 MHz) spectrometer. ¹³C NMR spectra were obtained in the pulsed FT mode at 75.0 MHz with a Bruker AC 300 spectrometer, and ²⁹Si NMR spectra were obtained at 59.6 MHz with a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per million (δ , ppm) with reference to Me₄Si (TMS).

MALDI-TOF Mass Spectrometry. The mass spectra reported in this article are MALDI TOF mass spectra. MALDI mass spectra were recorded with a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated at an accelerating potential of 20 kV in both linear and reflection modes. The mass spectra shown represent an average over 256 consecutive laser shots (3 Hz repetition rate). Peptides were used to calibrate the mass scale using the two-point calibration software 3.07.1 from PerSeptive Biosystems. Mentioned m/z values correspond to monoisotopic masses. The dendrimer solutions (10-3 M) were prepared in tetrahydrofuran (THF). Matrix compounds were from Sigma (France) and used without further purification. The matrixes, 2,5dihydroxybenzoic acid (2.5-DHB), 1,8-dihydroxy-9[10H]-anthracenone (dithranol), 6-azathiothymine, 2,4,6-trihydroxyacetophenone, 7-hydroxycoumarin, or 2-anthramine, were also dissolved in THF (10 g L⁻¹). One microliter of dendrimer solution was mixed with $50 \,\mu\text{L}$ of matrix solution. Ten microliters of alkali iodide (LiI, NaI) solution (5 g L^{-1} in THF) was added in some experiments to induce cationization. One microliter of the final solution was deposited onto the sample stage and allowed to dry in air.

Dynamic Light Scattering Measurements. The DLS measurements were made using a Malvern Zetasizer 3000 HSA instrument at 25 °C at an angle of 90°.

Cyclic Voltammetry Measurements. All electrochemical measurements were recorded under nitrogen atmosphere. Conditions: solvent, dry dichloromethane; temperature, 20 °C; supporting electrolyte, [*n*-Bu₄N][PF₆] 0.1 M; working and counter electrodes, Pt; reference electrode, Ag; internal reference, FeCp*₂ (Cp* = η^{5} -C₅Me₅); scan rate, 0.200 V s⁻¹.

Elemental Analyses. These were performed by the Center of Microanalyses of the CNRS at Lyon Villeurbanne, France.

General Hydrosilylation Reactions. The olefin compound, diethyl ether, the silane derivative (2 equiv per branch), and Kartsted catalyst (0.1%) were successively introduced into a Schlenk flask under a nitrogen atmosphere. The reaction solution was stirred at 25 °C for 16 h. The solvent was removed under vacuum, the catalyst residue was removed by flash chromatography with ether, and the solvent was removed.

General Synthesis of the Cobalticinium Dendrimers. The iodomethylsilane dendrimer, 14 (2 equiv per branch), and K_2CO_3 (10 equiv per branch) were introduced into a Schlenk flask, then dry DMF (30 mL) was added and the reaction mixture was heated at 80 °C for 48 h under magnetic stirring. After removing the solvent *in vacuo*, dichloromethane (20 mL) was added and the mixture was filtered on Celite to remove K_2CO_3 . The product was dissolved in methanol and after addition of KPF₆ a brown solid precipitated. The solution was filtrated on Celite, washed with methanol, and dissolved in CH₂Cl₂. After removing the solvent *in vacuo* a yellow solid was obtained.

Synthesis of [Cp*CoCp(CH₂)₉HC=CH₂][PF₆], 11. To a THF solution of pentamethylcyclopentadiene (1.88 mL, 12.0 mmol) was added dropwise 7.68 mL of a *n*-butyllithium solution (2.5 M), -60 °C, under a nitrogen atmosphere at -60 °C. After agitation for 30 min, a THF solution of CoCl₂ (1.548 g, 12.0 mmol) was added slowly at -60 °C (dark blue solution). After 1 h, a THF solution of 10 (2.633 g, 12.0 mmol), resulting from the deprotonation of the corresponding diene with *n*-butyllithium, was added, and the final brown solution was left under agitation for 16 h. After 5 h

under agitation, the solvent was removed under vacuum, the crude product was dissolved in water and filtered under Celite, and the aqueous solution was washed with ether. The product was then precipitated from water upon addition of an aqueous HPF₆ solution (24 mmol), and it was recovered by filtration and washed with ether. The product **11** was obtained as yellow oil in 25% yield (1.70 g).

¹H NMR (CDCl₃, 300 MHz): 5.77 (m, 1H, C*H*=CH₂), 4.96 (m, 6H, CH=C*H*₂ and C*H* of Cp), 2.17 (m, 2H, C*H*₂Cp), 1.99 (s, 15H, C*H*₃ of Cp^{*}), 1.69 (m, 2H, C*H*₂CH=CH₂), 1.29 (CH₂), ¹³C NMR (CDCl₃, 75.47 MHz): 139.1 (CH=CH₂), 114.1 (CH=CH₂), 104.6 (C_q of Cp), 96.8 (C_q of Cp^{*}), 86.3 and 84.6 (CH of Cp), 36.3 (CpCH₂), 33.7 (CH₂CH=CH₂), 29.3 ((CH₂)₇), 9.9 (CH₃ of Cp^{*}). MS (MALDI-TOF; *m/z*): calcd for C₂₆H₄₀Co⁺ 411.49, found 411.28. Anal. Calcd for C₂₆H₄₀Co⁺PF₆: C 56.12, H 7.24. Found: C 56.32, H 7.07.

Synthesis of $[Cp*CoCp(CH_2)_{11}Si(Me_2)CH_2Cl][PF_6]$, 12. Compound 12 was synthesized from 11 (1.09 g, 1.96 mmol) and (dimethyl)chloromethylsilane (0.439, 3.92 mmol) using the general procedure for hydrosilylation reactions (using THF as the solvent instead of ether). The catalyst residue was removed by flash chromatography on alumina using dichloromethane as the solvent. After removing the solvent, 0.8635 g of yellow oil was obtained (66% yield).

¹H NMR (CDCl₃, 300 MHz): 5.06 and 4.87 (d, 4H, *CH* of Cp), 2.71 (SiC*H*₂Cl), 2.12 (m, 2H, *CH*₂Cp), 1.94 (s, 15H, *CH*₃ of Cp*), 1.40 (s, 2H, *CH*₂CH₂Si), 1.19 (m, 14H, (*CH*₂)₈), 0.56 (s, 2H, CH₂CH₂Si), 0.032 (Si(*CH*₃)₂). ¹³C NMR (CDCl₃, 75.47 MHz): 104.7 (Cq of Cp), 96.8 (*C*q of Cp*), 86.2 and 84.6 (*C*H of Cp), 36.3 (CpCH₂), 33.8 (*C*H₂CH₂CH₂Si), 29.3 ((*C*H₂)₇), 25.9 (SiCH₂Cl), 23.4 (CH₂CH₂CH₂Si), 13.6 (CH₂CH₂CH₂Si), 9.9 (*C*H₃ of Cp*), -4.7 (Si(*C*H₃)₂). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm} : 3.70 (*Si*(CH₃)₂). MS (MALDI-TOF; *m*/*z*): calcd for C₂₉H₄₉ClSiCo⁺ 520.17, found 519.30. Anal. Calcd for C₂₉H₄₉ClCoF₆PSi: C 52.37, H 7.43. Found: C 53.49, H 7.43.

Synthesis of $[Cp*CoCp(CH_2)_{11}Si(Me_2)CH_2I][PF_6]$, 13. Compound 13 (0.8635 g, 1.29 mmol), NaI (0.581 g, 3.87 mmol), and butanone (50 mL) were introduced in a Schlenk flask. The reaction mixture was stirred at 80 °C for 16 h. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane (20 mL) and washed with a saturated aqueous solution of Na₂S₂O₃. This solution was dried with Na₂SO₄ and filtered, and the solvent was removed under vacuum. The product 13 was obtained as a yellow oil in 91% yield (0.891 g).

¹H NMR (CDCl₃, 300 MHz): 5.01 and 4.83 (d, 4H, *CH* of Cp), 2.11 (m, 2H, *CH*₂Cp), 1.88 (s, 15H, *CH*₃ of Cp*), 1.82 (SiC*H*₂I), 1.34 (s, 2H, *CH*₂CH₂Si), 1.12 (m, 14H, (CH₂)₇), 0.52 (s, 2H, CH₂C*H*₂Si), -0.0004 (Si(*CH*₃)₂). ¹³C NMR (CDCl₃, 75.47 MHz): 104.6 (*C*_q of Cp), 96.7 (*C*_q of Cp*), 86.2 and 84.6 (*C*H of Cp), 36.3 (Cp*C*H₂), 33.4 (*C*H₂CH₂CH₂Si), 29.4 ((*C*H₂)₇), 23.5 (CH₂CH₂CH₂Si), 14.7 (CH₂CH₂CH₂Si), 9.9 (*C*H₃ of Cp*), -3.06 (Si(*C*H₃)₂), -12.8 (Si*C*H₂I). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm} : 4.82 (*Si*(CH₃)₂).

Synthesis of Cp*CoCp(CH₂)₁₁Si(Me₂)CH₂OC₆H₄OH, 14. Compound 14 (0.891 g, 1.17 mmol), hydroquinone (0.644 g, 5.85 mmol), and K₂CO₃ (0.819 g, 5.85 mmol) were introduced into a Schlenk flask. Dry DMF (20 mL) was added, and the reaction mixture was heated at 80 °C for 48 h under magnetic stirring. After removing the solvent under vacuum, dichloromethane (20 mL) was added and the mixture was filtered on Celite in order to remove K₂CO₃. The solvent was removed under vacuum, and the product was precipitated with CH₂Cl₂/ethyl ether (5:95). Product 14 was obtained as a yellow waxy product in 74% yield (0.6436 g).

¹H NMR (CDCl₃, 300 MHz): 6.91 and 6.73 (d, 4H, *CH* arom.), 5.26 and 5.07 (d, 4H, *CH* of Cp), 3.49 (SiCH₂O), 2.20 (m, 2H, CH₂Cp), 2.05 (s, 15H, *CH*₃ of Cp*), 1.41 (s, 2H, *CH*₂CH₂Si), 1.19 (m, 14H, (CH₂)₈), 0.62 (s, 2H, CH₂CH₂Si), -0.0067 (Si(*CH*₃)₂). ¹³C NMR (CH₃COCH₃, 75.47 MHz): 155.7 (arom. *C*_q), 152.3 (arom. COH), 116.7 and 115.5 (arom. CH), 99.30 (C_q of Cp), 98.4 (C_q of Cp*), 87.3 and 86.5 (CH of Cp), 61.4 (SiCH₂O), 37.2 (CpCH₂), 34.3 (CH₂CH₂CH₂Si), 28.2 ((CH₂)₇), 24.4 (CH₂CH₂CH₂Si), 14.4 (CH₂CH₂CH₂Si), 10.6 (CH₃ of Cp*), -4.4 (Si(CH₃)₂). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm} : 0.35 (*Si*(CH₃)₂). MS (MALDI-TOF; *m/z*): calcd for C₃₅H₅₄O₂SiCo⁺ 593.78, found 593.31.

Synthesis of G₀-Co*, 15. The G₀-Co* metallodendrimer 15 was synthesized from 9-iodide dendrimer 2 (0.039 g, 0.0170 mmol), 14 (0.175 g, 0.237 mmol), and K₂CO₃ (0.274 g, 1.95 mmol) using the general synthesis for cobalticinium dendrimers. The product 15 was obtained as a yellow waxy product in 41% yield (0.054 g).

¹H NMR (CH₃COCH₃, 300 MHz), δ_{ppm} : 7.04 (s, 3H, CH core), 6.75 (d, 36H, arom), 5.25 and 5.15 (d, 36H, Cp), 3.46 and 3.41 (d, 36H, SiCH₂O), 2.30 (t, 18H, CH₂Cp), 1.99 (s, 135H, CH₃ of Cp*), 1.64 (s, 36H, $CH_2CH_2CH_2Si$), 1.19 (m, 144H, $(CH_2)_7$ and CH₂CH₂CH₂Si), 0.56 (s, 36H, CH₂CH₂CH₂Si), 0.00 and -0.044 (d, 108H, Si(CH₃)₂). ¹³C NMR (CH₃COCH₃, 62 MHz), δ_{ppm} : 155.3 (arom. OCq), 114.2 (arom. CH), 104.70 (Cq of Cp), 97.3 (Cq of Cp*), 89.2 and 84.6 (CH of Cp), 60.2 (OCH2Si), 44.0 (benzylic C_q), 35.9 (CH₂CH₂CH₂Si), 33.1 (CpCH₂), 28.2 ((CH₂)₇), 23.2 (CH₂CH₂CH₂Si), 13.2 (CH₂CH₂CH₂Si), 8.8 (CH₃ of Cp*), -5.7 $(Si(CH_3)_2)$. ²⁹Si NMR (CH₃COCH₃, 59.62 MHz), δ_{ppm} : 0.30 and $(Si(CH_3)_2)$. MS (MALDI-TOF; m/z): calcd 0.19 for [C378H606O18Si18C09]9+ 6 474.00, found 6 500. Anal. Calcd for C378H606O18Si18C09P9F54: C 58.36, H 7.85. Found: C 57.16, H 7.77.

Synthesis of G₅-Co*, 16. The G₅-Co* dendrimer 16 was synthesized from 2187-iodide dendrimer 7 (0.060 g, 0.0000621 mmol), 14 (0.161 g, 0.217 mmol), and K₂CO₃ (0.190 g, 1.36 mmol) using the general procedure for the synthesis of cobalticinium dendrimers. The product 16 was obtained as a yellow waxy product with 53% yield (0.069 g).

¹H NMR (CH₃COCH₃, 300 MHz), δ_{ppm} : 7.11 (d, *CH* arom.), 6.74 (d, OCq*CH* arom.), 5.18 (d, Cp), 3.47 and 3.40 (d, SiCH₂O), 2.28 (t, *CH*₂Cp), 1.99 (s, *CH*₃ of Cp*), 1.60 (s, *CH*₂CH₂CH₂Si), 1.17 (m, (*CH*₂)₇ and *CH*₂CH₂CH₂Si), 0.56 (s, *CH*₂CH₂CH₂Si), 0.0005 and -0.062 (d, Si(*CH*₃)₂). ¹³C NMR (CH₃COCH₃, 75 MHz), δ_{ppm} : 156.6 (arom. *C*qOCH₂Si), 147.8 (arom. *C*_q of the dendron), 127.2 and 113.4 (arom. *CH* of the dendron), 115.5 (arom. *CH*), 97.7 (*C*_q of Cp), 92.8 (*C*_q of Cp*), 87.3 and 85.8 (*CH* of Cp), 61.4 (OCH₂Si), 42.8 (benzylic *C*q), 34.4 (Cp*CH*₂), 31.6 (*CH*₂CH₂CH₂Si), 29.6 ((*CH*₂)₇), 25.5 (*CH*₂CH₂CH₂Si), 14.4 (*CH*₂CH₂CH₂Si), 10.1 (*CH*₃ of Cp*), -4.2 (Si(*CH*₃)₂). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm} : 0.31 and 0.098 (*Si*(Me)₂). Anal. Calcd for C₁₀₃₈₃H₁₆₆₁₃₄-O₅₄₆₃Si₅₄₆₃Co₂₁₈₇P₂₁₈₇F₁₃₁₂₂: C 59.35, H 7.97. Found: C 60.53, H 8.57.

Synthesis of G_6 -Co*, 17. The G_6 -Co* dendrimer 17 was synthesized from 6561-iodide dendrimer 8 (0.060 g, 0.0000379

mmol), 14 (0.280 g, 0.379 mmol), and K_2CO_3 (0.348 g, 2.48 mmol) using the general procedure for the synthesis of cobalticinium dendrimers. The product 17 was obtained as a yellow waxy product in 19% yield (0.040 g).

¹H NMR (CH₃COCH₃, 300 MHz), δ_{ppm} : 7.11 (d, *CH* arom), 6.74 (d, OCq*CH* arom.), 5.18 (d, Cp), 3.47 and 3.40 (d, SiCH₂O), 2.28 (t, *CH*₂Cp), 1.99 (s, *CH*₃ of Cp*), 1.60 (s, *CH*₂CH₂CH₂Si), 1.17 (m, (*CH*₂)₇ and CH₂CH₂CH₂Si), 0.56 (s, CH₂CH₂CH₂Si), 0.0005 and -0.062 (d, Si(*CH*₃)₂). ¹³C NMR (CH₃COCH₃, 75 MHz), δ_{ppm} : 156.6 (arom. *C*_qOCH₂Si), 147.8 (arom. *C*_q of the dendron), 127.2 and 113.4 (arom. CH of the dendron), 115.5 (arom. *CH*), 97.7 (*C*_q of Cp), 92.8 (*C*_q of Cp*), 87.3 and 85.8 (*C*H of Cp), 61.4 (OCH₂Si), 42.8 (benzylic *C*q), 34.4 (CpCH₂), 31.6 (*CH*₂CH₂CH₂Si), 10.1 (*CH*₃ of Cp*), -4.2 (Si(*CH*₃)₂). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm} : 0.31 and 0.098 (*Si*(Me)₂). Anal. Calcd for C₃₁₁₅₉₈H₄₉₈₅₅₈O₁₆₃₉₈Si₁₆₃₉₈Co₆₅₆₁F₅₉₃₆₆: C 59.35, H 7.97. Found: C 56.37, H 7.44.

Synthesis of G_7 -Co*, 18. The G_7 -Co* dendrimer 18 was synthesized from 19683-iodide dendrimer 9 (0.050 g, 0.00000786 mmol), 14 (0.204 g, 0.314 mmol), and K₂CO₃ (0.220 g, 1.57 mmol) using the general procedure for the synthesis of cobalticinium dendrimers. The product 18 was obtained as a yellow waxy product in 17% yield (0.025 g).

¹H NMR (CH₃COCH₃, 300 MHz), δ_{ppm} : 7.12 (m, arom.), 6.78 (m, arom), 5.28 (d, Cp), 3.53 and 3.44 (m, SiCH_2O), 2.31 (m, CH₂Cp), 1.95 (s, CH₃ of Cp*), 1.62 (s, CH₂CH₂CH₂Si), 1.29 (m, $(CH_2)_7$ and $CH_2CH_2CH_2Si$, 0.68 (s, $CH_2CH_2CH_2Si$), 0.012 (s, Si(CH₃)₂). ¹³C NMR (CH₃COCH₃, 75 MHz), δ_{ppm} : 156.5 (arom C_q OCH₂Si), 147.8 (arom. C_q of the dendron), 127.2 and 113.2 (arom. CH of the dendron), 115.3 (arom. CH), 97.6 (C_q of Cp), 92.7 (C_a of Cp*), 87.3 and 85.9 (CH of Cp), 61.4 (OCH₂Si), 42.7 (benzylic Cq), 34.4 (CpCH₂), 31.5 (CH₂CH₂CH₂Si), 29.6 ((CH₂)₇), 25.7 (CH₂CH₂CH₂Si), 14.4 (CH₂CH₂CH₂Si), 10.2 (CH₃ of Cp*), -4.3 (Si(CH₃)₂). ²⁹Si NMR (CDCl₃, 59.62 MHz), δ_{ppm} : 0.31 Anal. Calcd for $(Si(Me)_2).$ C₉₃₄₈₉₃H₁₄₉₅₈₃₀O₄₉₂₀₃Si₄₉₂₀₃-Co₁₉₆₈₃P₁₉₆₈₃F₁₁₈₀₉₈: C 59.35, H 7.97. Found: C 56.12, H 7.38.

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