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# 'Click' Synthesis and Redox Properties of Triazolyl Cobalticinium Dendrimers

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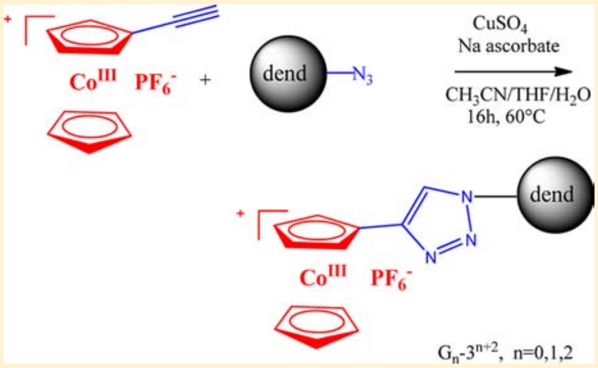
Ⓢ *Supporting Information*



**ABSTRACT:** The derivatization of macromolecules with redox-stable groups is a challenge for molecular electronics applications. The large majority of redox-derivatized macromolecules involve ferrocenes, and there are only a few reports with cobalticinium. We report here the first click derivatization of macromolecules with the cobalticinium redox group using ethynylcobalticinium hexafluorophosphate, **1**. Cu$^I$ catalysis was used for these selective click metallodendrimer syntheses starting from **1** and providing the tripodal dendron **3** that contains three 1,2,3-triazolylcobalticinium termini and a phenol focal point and the dendrimers of generations 0, 1, and 2 containing 9, 27, and 81 triazolylcobalticinium units for the dendrimers **4**, **5**, and **6**, respectively. Atomic force microscopy (AFM) statistical studies provided the progression of height upon increase of dendrimer generation. Cyclic voltammetry studies in MeCN and dimethylformamide (DMF) show the solvent-dependent reversibility of the Co$^{III/II}$ wave (18e/19e) and generation dependent reversibility of the Co$^{II/I}$ (19e/20e) wave in DMF. The $H_2PO_4^-$ anion is only recognized by the largest metallodendrimer **6** by a significant cathodic shift of the Co$^{III/II}$ wave.

## ■ INTRODUCTION

Cobalticinium salts[1] have been the subject of attention for their useful electrochemistry and electron-transfer chemistry. They present a relative stability of three oxidation states, including the 19-electron neutral cobaltocene[1,2] and the very electron rich 20-electron cobaltocene anion.[3] When redox-reversible transition-metal complexes are linked to nanosystems, they undergo chemically and electrochemically reversible transfer of a large number of electrons, and these multiple redox processes are useful for nanodevices behaving as nanobatteries,[4] redox sensing,[5] and biosensing,[6] modified electrode surfaces[7] and redox catalysis.[8] Poly cobalticinium receptors were extensively studied by Beer et al. for anion recognition,[5] and various cobalticinium polymers obtained either by ring-opening cobaltocenophane[9] or from cobalticinium carboxylic acid as a side group[10] have been reported.

Metallodendrimers have a rich chemistry that has been extensively reviewed.[11] The dendritic structures offer the opportunity of introduction of many redox centers at the periphery of the molecular frame, allowing multiple possibilities of functionalization.[12] This concept has been widely studied with ferrocene dendrimers.[13] However, cobalticinium dendrimers are much less developed even though they have been already reported by several groups.[14] These metallodendritic syntheses have systematically used cobalticinium carboxylic acid. Click methodology,[15] in particular the copper catalyzed azide−alkyne cycloaddition (CuAAC) forming 1,2,3 triazoles (trz),[16] however, has recently appeared as one of the most powerful and practical means to form such nanoassemblies.[17] Ferrocenyl dendrimers have been synthesized in this way,[18] and advantage of the introduction of trz ligands on the dendritic tethers has appeared as a powerful means to stabilize palladium[19] and gold[20] nanoparticles with remarkable catalytic[19] and sensor properties.[18]

Recently, complexes containing a single trz-cobalticinium unit have been synthesized from ethynylcobalticinium, verifying the possibility to link cobalticinium to other groups in this way by CuAAC click chemistry.[21] Herein we now report the use of the click CuAAC strategy using ethynyl cobalticinium to synthesize a metallodendron with 1→3 connectivity[22] and three generations (G0, G1, and G2) of cobalticinium dendrimers **4**, **5**, and **6** (Chart 1) with the same connectivity containing respectively 9, 27, and 81 cobalticinium termini. Cyclic voltammetry studies of these new redox-active metallodendrimers including redox recognition of the $H_2PO_4^-$ anion with positive dendritic effects[23] are also reported here.

## ■ RESULTS AND DISCUSSION

### 1. Synthesis of the Dendrimers Series and Phenol-triallyl Dendron.

The construction for the G0, G1, and G2 chloromethyl(dimethyl)silyl dendrimers with 1→3 connectivity[22] were synthesized as described previously upon CpFe$^+$-induced triallylation of mesitylene and *p*.methoxytoluene followed, after decomplexation, by hydrosilylation of the polyallyl dendritic cores and dendron using chloromethyldimethylsilane and iteration using a Williamson reaction with the

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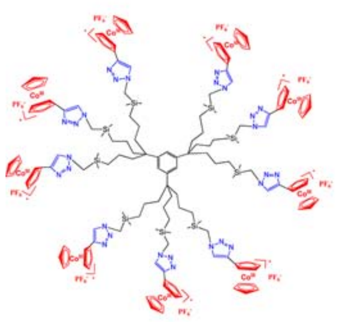
## Chart 1



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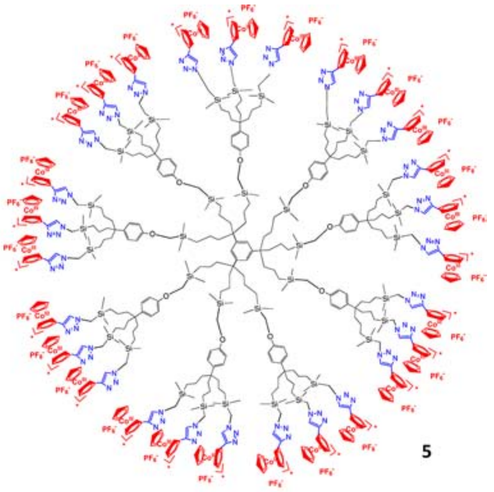

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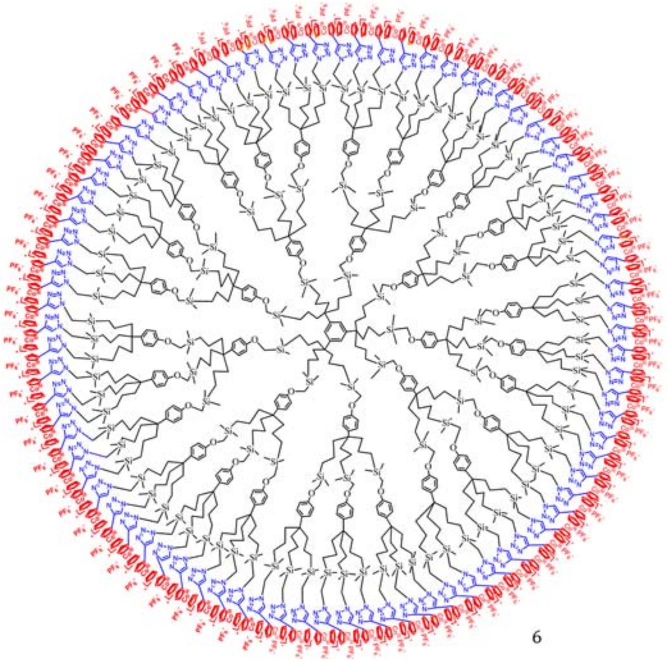

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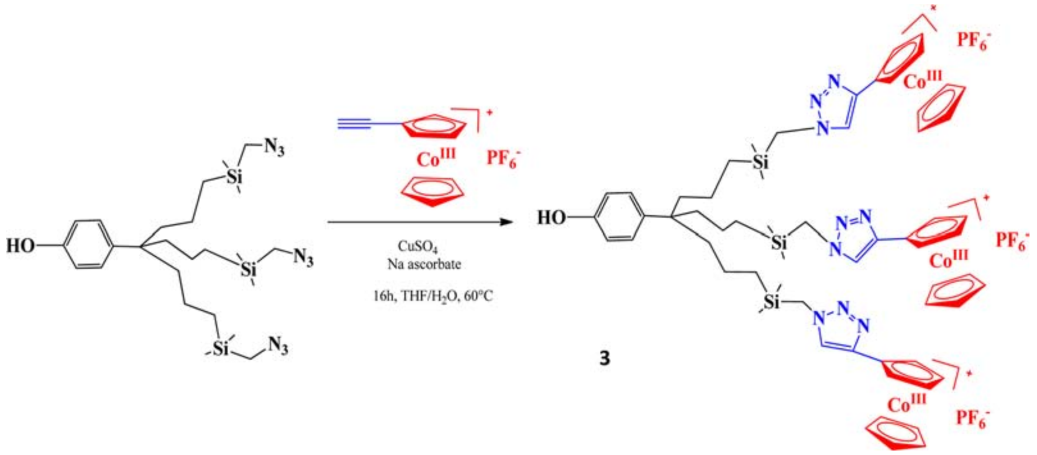
## Scheme 1. Click Synthesis of the tris-trz-Cobalticinium Phenoltriallyl Dendron 3



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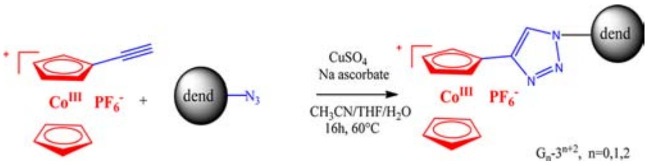
tribranched phenol dendron (phenol triallyl).[24] The terminal chloro groups were then substituted by azido groups by reaction with sodium azide providing azido-terminated dendrimers and dendron.[18]

**2. Click Synthesis of the Dendron and Dendrimers.** Ethynylcobalticinium **1** was synthesized as previously described in 60% overall yield from cobalticinium hexafluorophosphate.[25] The uncatalyzed Huisgen reaction[26] between **1** and benzyl azide conducted in the absence of copper catalyst in 1,2 dimethoxyethane at 80 °C was completed in 2 days giving 92% of the 1−4 disubstituted triazole **2** (**a**) and only 8% of the 1−5 disubstituted triazole **2** (**b**) (see Supporting Information). The selectivity for the 1−4 isomer is remarkable under these conditions; it is likely due to steric reasons favoring the 1−4 substitution.[23] The mixture of isomers was characterized by $^1$H, $^{13}$C, and $^{31}$P NMR, IR, UV−vis, and ESI mass spectrometry. Comparing to the CuAAC click reaction with the use of copper catalyst ($CuSO_4$ + ascorbic acid), however, the latter does not give isomerization at all, but only the 1−4 disubstituted trz product, and the reaction is much more rapid. Consequently, the catalyzed CuAAC reaction of **1** with the azido-terminated dendron and dendrimers was appropriate for the metallodendrimer assembly. Thus the syntheses of the trz-cobalticinium dendron **3** and dendrimers **4**, **5**, **6** were carried out using $CuSO_4$/sodium ascorbate between the terminal alkyne **1** and the tris-azido phenoltriallyl dendron (Scheme 1) and three generations G0, G1, and G2 of dendrimers dend-$N_3$ containing 3, 9, 27, 81 azido termini respectively (Scheme 2). The solvents in each reaction were chosen to achieve the solubility of the final product, because the polycationic cobalticinium dendrimers were soluble only in high polarity solvents, the reaction of the dendron was carried out in THF/$H_2O$, that of **4** in $CH_3CN$/$H_2O$ and those of **5** and **6** in a mixture of THF/$CH_3CN$/$H_2O$, because the azido-terminated precursors were not soluble in $CH_3CN$. The temperature of the reaction was 60 °C, and the reactions were left stirring during 16 h. The reactions needed stoichiometric rather than catalytic amounts of $Cu^I$ because of encapsulation of $Cu^I$ by coordinating to the resulting trz ligand, as previously encountered with ferrocenyl analogues.[18,27] The copper salt was finally removed as $[Cu(NH_3)_2(H_2O)_2]$ $[SO_4]$ by adding an aqueous solution of $NH_3$ that was left stirring for 15 min. The resulting tris-trz-cobalticinium terminated dendron and trz-cobalticinium dendrimers were purified, after workup, by precipitation in diethyl ether as orange powder. They were isolated as orange-red products in high yields. They were characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR, IR, UV−vis., DOSY NMR, MALDI-TOF mass spectrometry, AFM measurements, cyclic voltammetry, and elemental analysis.

**Scheme 2. Click Synthesis of the Dendrimers 4, 5, and 6 with 9, 27, and 81 trz-Cobalticinium Termini, Respectively**



**3. Characterizations.** The characterization of the dendritic cobalticinium salts depends on their solubility that varies with the number of cobalticinium moieties in the molecule. The trz-cobalticinium group is very hydrophilic, and it is soluble only in polar solvents. As the number of trz-cobalticinium groups increases in a molecule, the polarity of the solvent in which it can be solubilized also increases. Indeed the monomers **2** (**a**), **2** (**b**) can be dissolved in dichloromethane, tetrahydrofuran (THF), acetone, acetonitrile, and DMF, whereas the dendrimer **6** can be solubilized only in very polar solvents such as $CH_3CN$, DMF, and DMSO. The solubility of the products is summarized in Table 1.

**Table 1. Solubilities of the trz-Cobalticinium Hexafluorophosphate Derivatives 2 (a), 3, 4, 5, and 6 as a Function of the Number of trz-Cobalticinium Termini, at 25°C**[a]

| product | $CH_2Cl_2$ | THF | acetone | $CH_3CN$/DMF |
|---|---|---|---|---|
| **2** (a) | + | + | + | + |
| **3** | − | + | + | + |
| **4** | − | − | + | + |
| **5** | − | − | + | + |
| **6** | − | − | − | + |

[a] +: very soluble; −: insoluble.

*The infrared spectra* are a very useful tool to monitor the click reactions, because the characteristic peak of the azido groups at about 2094 cm$^{-1}$ disappears at the end of the reactions confirming that the azido groups are replaced by the 1,2,3-triazole groups. The characteristic absorption of the $PF_6$ anion of these trz-cobalticinium products shows a strong band in the range 836−838 cm$^{-1}$. The absorptions due to the =C−H stretching of the triazole and Cp groups of the trz-cobalticinium unit are found in the range 3118−3127 cm$^{-1}$ (Figure 1).

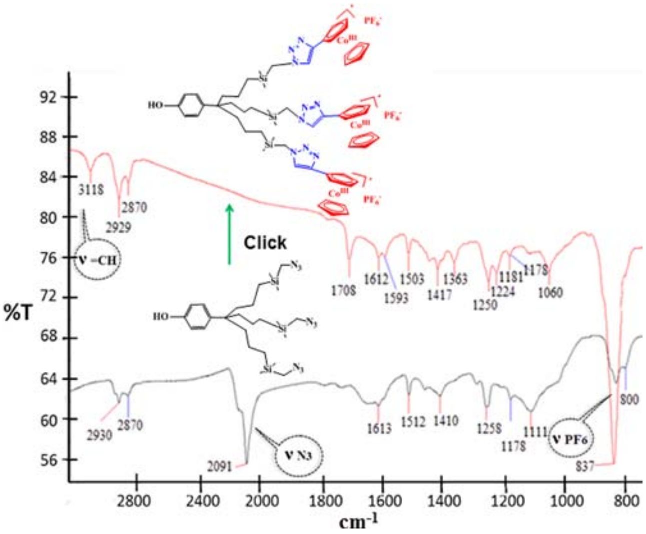


**Figure 1.** IR spectra of the tris-azido phenoltriallyl precursor and product **3** after the CuAAC click reaction.

*NMR spectroscopy* confirms the structure of the trz-cobalticinium products. Particularly, in $^1$H NMR the formation of the trz ring is clearly shown by the appearance of the peaks around 8.4 ppm (in $CD_3COCD_3$) for the products **3**, **4**, and **5**, and around 8.0 (in $CD_3CN$) for the product **6**. In all the cases, the peak of Si$CH_2$-$N_3$ at 2.7−2.8 ppm has disappeared, whereas the appearance of the new peak of Si*CH*$_2$-trz takes place at about 4.1 ppm. The presence of the trz group is also confirmed by the appearance of the characteristic peaks of *Cq* and CH of trz as well as Si$CH_2$-trz in the $^{13}$C NMR spectra. The $^{29}$Si NMR spectra of the dendrimers are very simple, showing one peak at 3.41 ppm (compounds **4** and **5**) and 3.50 ppm (compound **6**) for *Si*$CH_2$-trz and another smaller peak at 0.46 ppm that corresponds to *Si*$CH_2$O for compounds **5** and **6**. Finally, the

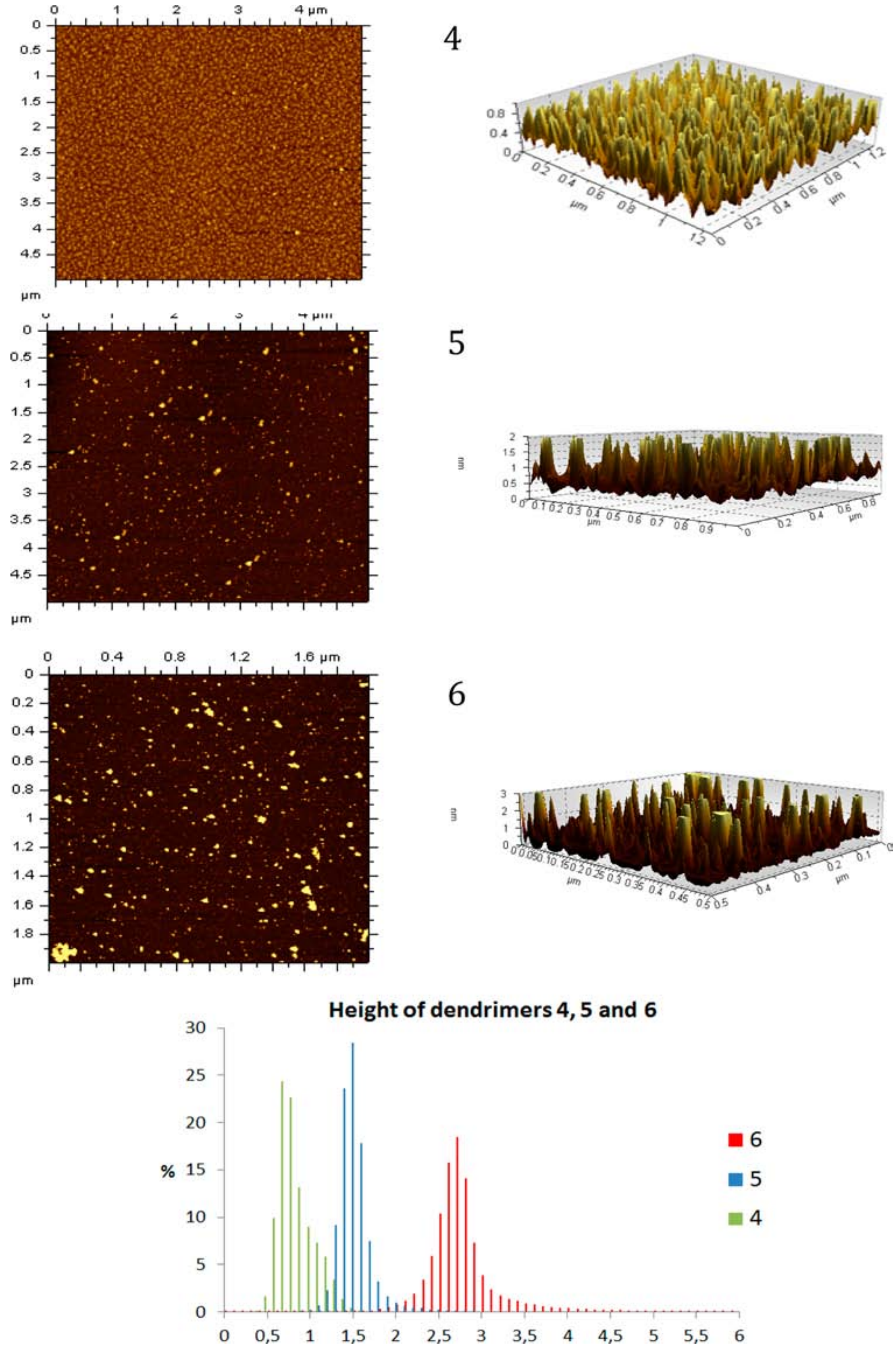


**Figure 2.** AFM images and statistical height distribution of dendrimers **4**, **5**, and **6**.

assignments of the number of protons in $^{1}$H NMR show the expected ratio between the dendritic frame part and the cobalticinium part, including for the large dendrimer **6**.

*Maldi-TOF mass spectrometry* confirms the structure of the positively monocharged trz-cobalticinium dendron **3** (showing two $PF_6$ anions) and trz-cobalticinium dendrimer **4** (see Supporting Information). *Elemental analysis* also confirms the structures of **3**, **4**, **5**, and **6**.

*UV–visible Spectroscopy.* A strong absorption band is observed for all the dendrimers in the ultraviolet region peaking at 354.8 nm, whereas a less intense absorption shoulder is observed in the visible region peaking at about 427 nm. From the Lambert–Beer's law, we calculated the molar extinction coefficient $\varepsilon$ for the compounds **3**, **4**, **5**, and **6**. Its value increases upon increase of dendrimer generation, which also confirms the progressivity of the trz-cobalticinium generations (**3**, **4**, **5**, and **6**). (For $\varepsilon$ values: see the Supporting Information)

*DOSY* (diffusion-ordered spectroscopy) experiments were carried out for the dendrimers **4**, **5**, and **6**. The main goal of these experiments was to measure the diffusion coefficient $D$ that was extracted from the DOSY $^1H$ NMR spectra. The latter also reflect the purity of the products. For compound **4**, the average diffusion coefficient value obtained is $D = 2.85\ (\pm 0.1) \times 10^{-6}\ cm^2/s$. In the case of the dendrimer **5** (27 branches), the calculated diffusion coefficient is $D = 2.58\ (\pm 0.1) \times 10^{-6}\ cm^2/s$, whereas in the case of the dendrimer **6** (81 branches), the calculated diffusion coefficient is $D = 6.46\ (\pm 0.1) \times 10^{-7}\ cm^2/s$.

In an effort to better characterize the three polycobalticinium dendrimers and their interaction with surfaces, and obtain a clearer evidence of the size progression, atomic force microscopy (AFM) studies have been conducted. Freshly cleaved mica surfaces (that have a negative surface charge density) have been used as clean imaging substrates. A diluted acetonitrile solution of each dendrimer was deposited on a mica surface by spin-coating (800−1000 rpm for one minute, 0.1% w/w). In their condensed phase, the dendrimers collapse onto the mica surface. The height of the dendrimer layer usually represents a monolayer, and the dendrimers agglomerate in large packages of variable sizes on the surface.[13] In our studies, the heights of the dendrimers were quite uniform. Therefore, statistical study of the height of each dendrimer by AFM analysis was obtained and provided a clear evidence of the size progression upon increase of dendrimer generation. (Figure 2).

Although both the DOSY $^1H$ NMR and AFM experiments yield dendrimer sizes, the two methods are not comparable, because the former provides a diameter that includes peripheral solvation or/and even eventually dendritic agglomerates in solution, whereas the latter gives the height (thicknesses) of a collapsed dendrimer in the condensed phase. The reproducible DOSY measuments indicated above leads to diameters of 4.8 nm for **4**, 5.6 nm for **5**, and 19.6 nm for **6** that are much larger than the AFM thicknesses indicated in the condensed phase for the reasons indicated above. In the present case, it is highly probable that interdendrimer ion-pairing intervenes for the formation of agglomerates in solution given the charged branch termini of the dendrimers, which increases the observed DOSY sizes in solution.

**4. Cyclic Voltammetry Studies.** The tris-triazolyl cobalticinium dendron **3** and the three generations of triazolyl-cobalticinium dendrimers (compounds **4**, **5**, and **6**) were studied by cyclic voltammetry using decamethylferrocene as the internal reference.[28] The cyclic voltammograms (CVs) were recorded in acetonitrile and DMF, a good solubility being accessible with both solvents, and the results are gathered in Table 2. The first reduction wave of all the products corresponds to the reduction of cobalticinium to the 19-electron complex cobaltocene ($Co^{III/II}$), and the second wave corresponds to the reduction of cobaltocene to the 20-electron cobaltocenyl anion ($Co^{II/I}$). Both waves are single in acetonitrile and DMF, which can be explained by the weakness of the electrostatic factor between the redox sites of the metallodendrimers, these redox centers being far from one another and separated by long tethers.[29]

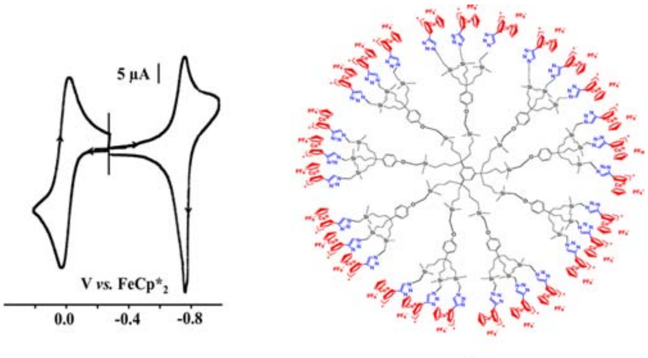
The first wave in both acetonitrile and DMF appears chemically and electrochemically reversible, a result similar to that obtained with the monomeric complex **2 (a)**.[21] The electrochemical reversibility involving equally all the redox groups is due to very fast rotation within the electrochemical time scale, where all the redox groups come close to the electrode provoking fast electron transfer between all the redox groups and the electrode,[30] and/or the electron-hopping mechanism.[31]

Adsorption during the cyclic voltammetry recording of dendrimer is common, and it is more marked with cationic dendrimers than with neutral ones. It is observed for the first wave only in acetonitrile, and it is marked for the high dendrimer generations. This large adsorption phenomenon for the large dendrimers is due to the low solubility of the reduced neutral dendrimer in acetonitrile. The monomer and dendron compounds **2 (a)** and **3** do not adsorb on the electrode. Adsorption begins with the nona-cobalticinium dendrimer **4** ($i_a/i_c$ =1.1) and gradually increases as the generation number of dendrimer increases. In particular, the $i_a/i_c$ value for dendrimers **5** (Figure 3) and **6** is 2.0 and 2.7 respectively (Table 2).

**Table 2. Redox Potentials and Chemical ($i_a/i_c$) and Electrochemical ($E_{pa} - E_{pc} = \Delta E$) Reversibility Data for Compounds 2(a)−6**[a]

| | | $Co^{III/II}$ [V] | | | $Co^{II/I}$ [V] | | |
|---|---|---|---|---|---|---|---|
| | solvent | $E_{1/2}$ | $\Delta E$ | $i_a/i_c$ | $E$ | $\Delta E$ | $i_a/i_c$ |
| **2 (a)**[21] | MeCN | −0.75 | 0.060 | 1.0 | $E_p = -1.76$ | 0 | 0 |
| **3** | MeCN | −0.78 | 0.040 | 0.6 | $E_p = -1.72$ | 0 | 0 |
| **3**[b] | MeCN | −0.78 | 0.060 | 1.0 | | | |
| **3** | DMF | −0.81 | 0.060 | 0.3 | $E_p = -1.81$ | 0 | 0 |
| **4** | MeCN | −0.74 | 0.030 | 0.5 | $E_{1/2} = -1.65$ | 0.050 | 0.2 |
| **4**[b] | MeCN | −0.74 | 0.065 | 1.1 | | | |
| **4** | DMF | −0.81 | 0.060 | 0.7 | $E_{1/2} = -1.79$ | 0.070 | 0.8 |
| **5** | MeCN | −0.75 | 0.015 | 0.3 | $E_{1/2} = -1.80$ | 0.010 | 0.3 |
| **5**[b] | MeCN | −0.75 | 0.010 | 2.0 | | | |
| **5** | DMF | −0.82 | 0.060 | 0.9 | $E_{1/2} = -1.77$ | 0.060 | 1 |
| **6**[b] | MeCN | −0.72 | 0.030 | 2.7 | | | |
| **6** | DMF | −0.82 | 0.040 | 0.9 | $E_{1/2} = -1.78$ | 0.050 | 0.7 |
| **6**[b] | DMF | −0.82 | 0.040 | 1.0 | | | |

[a] Supporting electrolyte: $[n\text{-}Bu_4N][PF_6]$ 0.1M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: $FeCp^*_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$); scan rate: 0.200 V $s^{-1}$. [b] Scanning until −1.0 V.



**5**

**Figure 3.** CV of **5** in $CH_3CN$. The wave at 0.0 V corresponds to the internal reference $FeCp^*_2$. Solvent: $CH_3CN$; reference electrode: Ag; working and counter electrodes: Pt; scan rate: 0.2 V/s; supporting electrolyte: $[n\text{-}Bu_4N][PF_6]$.

The second wave for compound **3** is completely irreversible just like for the monomer **2 (a)**, whereas in dendrimers (**4**, **5**, and **6**) the situation changes. In acetonitrile, this second wave is reversible at the electrochemical time scale but chemically irreversible. This is due to partial degradation of the dendritic products during reduction ($Co^{II/I}$), caused by population of antibonding $e^*_1$ orbitals, which destabilizes the cobalt-ligand bonds in synergy with the solvent interaction.[32] This thermodynamic destabilization is indeed combined with kinetic destabilization when the solvent is a ligand that can easily displace the Cp ring, which is especially the case with MeCN. This chemical irreversibility is responsible for the appearance of a shoulder at the anode of the first wave during oxidation. Upon scanning until less negative potentials in the same solvent, the first $Co^{III/II}$ wave is completely reversible, and no splitting is observed (Figure 4), showing that decomposition of the Co complex does not occur at the 19-electron level, but only upon scanning the 20-electron state. However, in DMF such degradation does not take place as the second wave appears both chemically and electrochemically reversible (Figure 5). Another observation is that the envelope of the first redox wave is broad, whereas in the $Co^{II/I}$ wave that does not contain cationic species this phenomenon does not appear. Thus the broad first wave could be due to electrostatic interactions differentiating the various single electron-transfer steps, that is, the electrostatic interaction for the first electron transfer involves all the cationic charges, whereas that for the last electron transfer involves only one positive charge for the whole dendrimer. Interactions between the cationic centers and the counteranions and the solvent molecules are responsible for the variation of the energy engaged in the heterogeneous electron transfers.

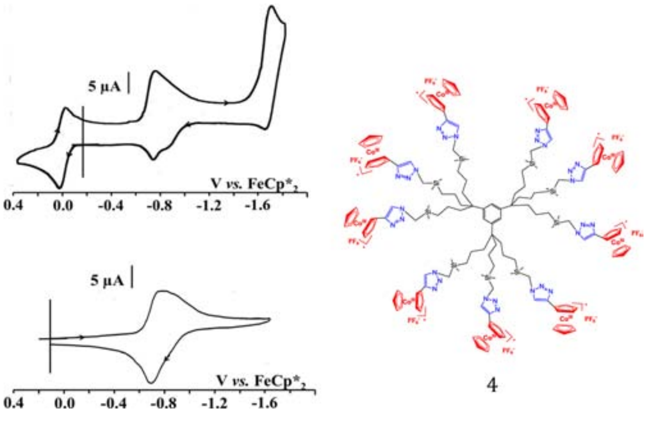


**Figure 4.** CV of **4** in $CH_3CN$. The wave at 0.0 V corresponds to the internal reference $FeCp^*_2$. Solvent: $CH_3CN$; reference electrode: Ag; working and counter electrodes: Pt; scan rate: 0.2 V/s; supporting electrolyte: $[n\text{-}Bu_4N][PF_6]$.

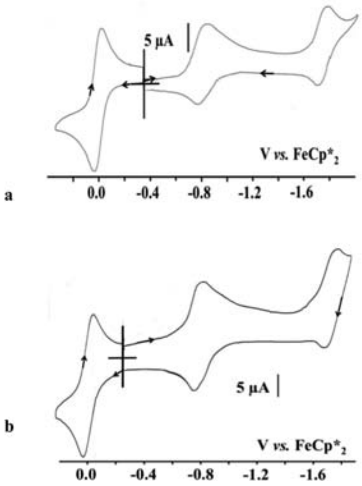


**Figure 5.** (a) CV of **4** in DMF. (b) CV of **5** in DMF. The wave at 0.0 V corresponds to the internal reference $FeCp^*_2$. Solvent: DMF; reference electrode: Ag; working and counter electrodes: Pt; scan rate: 0.2 V/s; supporting electrolyte: $[n\text{-}Bu_4N][PF_6]$.

*Redox recognition* of anions by cyclic voltammetry is possible with the triazolylcobalticinium dendrimers. Recognition and sensing of anions are of importance in many fields, ranging from environmental monitoring, biology, and industrial applications to clinical diagnostics. To investigate this property, the recognition of the $H_2PO_4$ anion as its $n\text{-}Bu_4N^+$ salt was probed. Such redox recognition has been first studied by Beer's group with polycobalticinium endoreceptors,[4] and extended by our group to dendritic exoreceptors.[23] Indeed, its addition to the electrochemical cell containing compound **6** provokes a splitting of the $Co^{III/II}$ CV wave for which the new part resulting from the addition of $[n\text{-}Bu_4N][H_2PO_4]$ is found at a potential 0.15 V more negative than the original one (Figure 6). The electrostatic binding of the anionic guest partly masks the positive charge, rendering the positively charged cobalticinium moiety more difficult to reduce to its neutral 19-electron form. Overall, the reasons for redox recognition combine the electrostatic and supramolecular interaction with dendritic (exoreceptor) effect. The supramolecular interactions are those of the hydrogen bonding between the OH groups of the $H_2PO_4^-$ anion and the nitrogen atoms of the trz group and eventually the interaction of oxygen atoms of the anion with the positively charged cobalt center (or eventually a chelating interaction involving both the trz and the Co center). The combined electrostatic and supramolecular interactions are not sufficient, however, to induce redox recognition in the present case (as in others involving monomers and small dendrimers), as demonstrated by the lack of redox recognition here with the trz-cobalticinium **2** (**a**), **3**, **4**, and **5**. A significant topological effect is required in synergy with the electrostatic and supramolecular effect to recognize the oxo-anions. This strong dendritic effect (i.e., the effect increases as the dendrimer generation increases) is only obtained here with the second-generation metallodendrimer **6**, whereas interestingly it is insufficient with the zeroth and first-generation dendrimers **4** and **5**. This confirms the positive dendritic effect in redox recognition, that is, the recognition improves as the dendrimer generation increases (note that we believe that in homogeneous catalysis, the dendritic effect with dendrimers terminated with catalysts is negative for steric reasons[33]). These trz-cobaticinium dendrimers are not adequate for $H_2PO_4^-$ anion titration, however, because the exact number of equivalents of the anion could not be calculated because of some precipitation occurring during addition of $[n\text{-}Bu_4N][H_2PO_4]$.

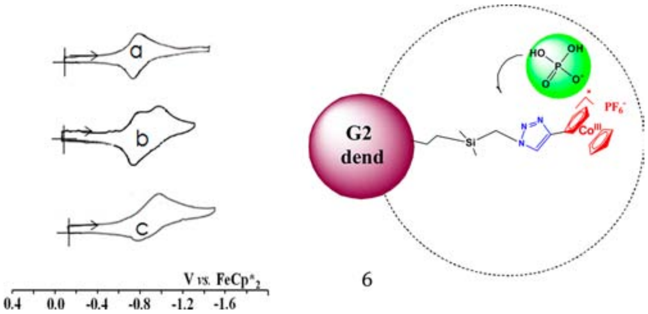


**Figure 6.** CVs of compound **6**: (a) In DMF, $[n\text{-}Bu_4N][PF_6]$ 0.1M; see Table 2 for data and conditions; (b) splitting of the reduction CV wave upon addition of $Bu_4NH_2PO_4$; (c) complete disappearance of the first wave upon addition of $Bu_4NH_2PO_4$.

## ■ CONCLUDING REMARKS

The paucity of cobalticinium chemistry has largely favored the development of ferrocene-containing dendrimers and polymers.

The great interest in polycationic dendrimers and polymers has recently led to research on cobalticinium polymers especially favored by the cobaltocenophane ring-opening polymerization and the use of cobalticinium-carboxylic acid. Click chemistry introduced a decade ago was ideal for the synthesis of cobaltocenyl dendrimer and polymers, which has been achieved for dendrimers in this article. The redox-active click cobalticinium dendrimers also benefit from the location of a 1,2,3-triazolyl (trz) ring attached to the cobalticinium group. Previous work has shown the interest of the trz ring as a ligand that was very useful for the stabilization of catalytically active nanoparticles[19] in metallodendrimers and for sensing.[17] Thus the present click metallodendrimers that are the first cobalticinium dendrimers benefit from both the trz unit attached to the cobalticinium redox group allowing facile redox recognition of substrates interacting with this heterocycle and the positive charge on each dendrimer termini that should enable further supramolecular anion design and ion-pair interaction. These systems will thus serve as a basis for further research in these directions as well as the development of soft materials of interest. Reduction studies of the trz-cobalticinium monomers involving 19-electron species[34] should also be extended to trz-cobalticinium dendrimers and polymers to search for molecular battery materials. Such studies are currently underway in our laboratory.

## ■ EXPERIMENTAL SECTION

**General Data.** For general data including solvents, apparatuses, compounds, reactions, spectroscopies, and CV, see the Supporting Information. G*n* indicates the generation number *n*. The mononuclear compound **1** was synthesized according to ref 25.

**General Procedure for the Click Synthesis of Polycobalticinium Dendron and Dendrimers.** The compound **1** (1.5 equiv per branch) and the azido-terminated dendron or dendrimers (**3**, **4**, **5**, or **6**) were dissolved in degassed THF, $CH_3CN$ or both, then degassed water was added and the reaction mixture was cooled to 0 °C. Then, an aqueous solution of $CuSO_4$ 1 M (1.1 equiv per branch) was added dropwise, followed by the dropwise addition of a freshly prepared solution of sodium ascorbate (2.2 equiv per branch) The color of the solution changed from orange to dark red upon addition of sodium ascorbate. The reaction mixture was allowed to stir for 16 h at 60 °C under nitrogen atmosphere. Then, the mixture of solvents was removed under vacuum, and 100 mL of nitromethane was added followed by the addition of an aqueous solution of ammonia. The mixture was allowed to stir for 15 min to remove all the copper salt trapped inside the dendron or dendrimer. The organic phase was washed twice with water, dried over sodium sulfate, filtered, and the solvent was removed under vacuum. Then the product was washed with THF to remove the excess of alkyne and precipitated from an acetone or acetonitrile solution in diethyl ether.

**Tris-triazolylcobalticinium Dendron 3.** The synthesis was carried out from ethynylcobalticinium **1** (406 mg, 1.134 mmol) and tris-azido phenoltriallyl dendron (144.6 mg, 0.252 mmol) using the above general procedure for click synthesis. The reaction was carried out in 60 mL of THF−40 mL of $H_2O$. The product **3** was obtained as an orange-red powder (400 mg). Yield: 96% $^1$H NMR (1D 1H), ($CD_3COCD_3$, 400 MHz): $\delta_{\mathrm{ppm}}$: 8.39 (3H, C*H* of trz), 7.15 and 6.78 (4H, C*H* arom.), 6.42 (6H, C*H* of Cp sub.), 6.03 (6H, C*H* of Cp sub.), 5.73 (15H, C*H* of Cp), 4.12 (6H, $\mathrm{SiC}\mathit{H}_2$-trz), 1.67 (6H, $C\mathit{H}_2CH_2CH_2Si$), 1.18 (6H, $CH_2C\mathit{H}_2CH_2Si$), 0.67 (6H, 18H, $CH_2CH_2C\mathit{H}_2Si$), 0.11 (18H, $\mathrm{Si}(C\mathit{H}_3)_2$). $^{13}$C NMR (1D 1H), ($CD_3COCD_3$, 75 MHz): $\delta_{\mathrm{ppm}}$: 155.74 (*Cq*OH), 138.34 (*Cq*-trz), 128.14 and 115,63 (CH arom.), 125.77 (CH of trz), 97.02 (*Cq* of Cp sub.), 86.69 (CH of Cp), 85.29 (CH of Cp sub.), 81.52 (CH of Cp sub.), 43.74 ($CqCH_2CH_2CH_2Si$), 42.50 $\mathit{Cq}CH_2CH_2CH_2Si$), 41.67 (trz-$CH_2Si$), 18.14 ($CqCH_2CH_2CH_2Si$), 15.20 ($CqCH_2CH_2CH_2Si$), −3.82 ($\mathrm{Si}(CH_3)_2$). MALDI-TOF-MS (*m*/*z*) of $C_{61}H_{77}Si_3N_9Co_3(PF_6)_2$: calc. 1503.29; found 1503.35. Anal. Calc. for $C_{61}H_{77}Si_3N_9Co_3(PF_6)_3(C_4H_8O)$: C 45.81, H 5.03; found: C 46.05 H 4.93.

**Dendrimer 4.** The synthesis was carried out from ethynylcobalticinium **1** (252 mg, 0.705 mmol) and G0−9$N_3$ (79.1 mg, 0.052 mmol) using the general procedure for click synthesis above. The reaction was carried out into 20 mL of $CH_3CN$−5 mL of $H_2O$. Product **4** was obtained as an orange-red powder (239 mg). Yield: 97% $^1$H NMR (1D 1H), ($CD_3COCD_3$, 400 MHz): $\delta_{\mathrm{ppm}}$: 8.39 (9H, C*H* of trz), 7.14 (3H, C*H* of arom.core), 6.39 (18H, C*H* of Cp sub.), 5.99 (18H, C*H* of Cp sub.), 5.70 (45H, C*H* of Cp), 4.12 (18H, $\mathrm{SiC}\mathit{H}_2$-trz), 1.76 (18H, $C\mathit{H}_2CH_2CH_2Si$), 1.23 (18H, $CH_2C\mathit{H}_2CH_2Si$), 0.71 (18H, 18H, $CH_2CH_2C\mathit{H}_2Si$), 0.10 (54H, $\mathrm{Si}(C\mathit{H}_3)_2$). $^{13}$C NMR (1D 1H), ($CD_3COCD_3$, 75 MHz): $\delta_{\mathrm{ppm}}$: 146.72 (*Cq* of arom.core), 138.41 (*Cq* of trz), 125.92 (CH of trz), 122.58 (CH of arom.core), 97.21 (*Cq* of Cp sub.), 86.78 (CH of Cp), 85.39, 81.59 (CH of Cp sub.), 44.84 ($CqCH_2CH_2CH_2Si$), 42.63 ($\mathit{Cq}CH_2CH_2CH_2Si$), 41.87 (trz-$CH_2Si$), 18.53 ($CqCH_2CH_2CH_2Si$), 15.56 ($CqCH_2CH_2CH_2Si$), −3.51 ($\mathrm{Si}(CH_3)_2$). $^{29}$Si NMR ($CD_3COCD_3$, 79.5 MHz): $\delta_{\mathrm{ppm}}$: 3.41 (9Si, *Si*$CH_2$trz). MALDI-TOF-MS (*m*/*z*) of $C_{171}H_{225}Si_9N_{27}Co_9(PF_6)_2$: calc. 3729.0; found 3729.1. Anal. Calc. for $C_{171}H_{219}Si_9N_{27}Co_9(PF_6)_9$: C 43.32, H 4.66; found: C 43.59 H 4.82.

**Dendrimer 5.** The synthesis was carried out from ethynylcobalticinium 1 (232 mg, 0.648 mmol) and G1-27$N_3$ (100.0 mg, 0.016 mmol) using the general procedure for click synthesis above. The reaction was carried out into 15 mL of $CH_3CN$−20 mL of THF and 5 mL of $H_2O$. Product **5** was obtained as an orange powder (202 mg). Yield: 80% $^1$H NMR (1D 1H), ($CD_3COCD_3$, 400 MHz): $\delta_{\mathrm{pmp}}$: 8.37 (27H, C*H* of trz), 7.23, 6.91 (39H, C*H* of arom.core), 6.38 (54H, C*H* of Cp sub.), 5.97 (54H, C*H* of Cp sub.), 5.67 (135H, C*H* of Cp), 4.10 (54H, $\mathrm{SiC}\mathit{H}_2$-trz), 3.60 (18H, $\mathrm{SiC}\mathit{H}_2O$), 1.66 (72H, $C\mathit{H}_2CH_2CH_2Si$), 1.20 (72H, $CH_2C\mathit{H}_2CH_2Si$), 0.66 (72H, 18H, $CH_2CH_2C\mathit{H}_2Si$), 0.08 (216H, $\mathrm{Si}(C\mathit{H}_3)_2$). $^{13}$C NMR (1D 1H), ($CD_3COCD_3$, 75 MHz): $\delta_{\mathrm{ppm}}$: 160.05 (arom. O*Cq*), 139.76 (*Cq* of trz), 138.40 (*Cq* of arom.core), 128.02 and 114.34 (arom. CH), 125.92 (CH of trz), 97.35 (*Cq* of Cp sub.), 86.66 (CH of Cp), 85.27, 81.44 (CH of Cp sub.), 60.81 ($CH_2OAr$), 43.97 ($CqCH_2CH_2CH_2Si$), 42.77 ($\mathit{Cq}CH_2CH_2CH_2Si$), 41.67 (trz-$CH_2Si$), 18.26 ($CqCH_2CH_2CH_2Si$), 15.33 ($CqCH_2CH_2CH_2Si$), −3.78 ($\mathrm{Si}(CH_3)_2$). $^{29}$Si NMR ($CD_3COCD_3$, 79.5 MHz): $\delta_{\mathrm{ppm}}$: 0.46 (9 Si, *Si*$CH_2O$), 3.41 (27Si, *Si*$CH_2$trz). Anal. Calc. for $C_{612}H_{786}Si_{36}N_{81}Co_{27}O_9(PF_6)_{27}$: C 46.11, H 4.97; found: C 45.98 H 5.12.

**Dendrimer 6.** The synthesis was carried out from ethynylcobalticinium 1 (218 mg, 0.608 mmol) and G2-81$N_3$ (100.0 mg, 0.005 mmol) using the general procedure for click synthesis above. The reaction was carried out into 15 mL of $CH_3CN$−20 mL of THF and 5 mL of $H_2O$. Product **6** was obtained as an orange powder (175 mg). Yield: 73% $^1$H NMR (1D 1H), ($CD_3CN$, 400 MHz): $\delta_{\mathrm{ppm}}$: 8.04 (81H, C*H* of trz), 7.15, 6.82 (147H, C*H* arom.), 6.16 (162H, C*H* of Cp sub.), 5.74 (162H, C*H* of Cp sub.), 5.48 (405H, C*H* of Cp), 3.98 (162H, $\mathrm{SiC}\mathit{H}_2$-trz), 3.50 (72H, $\mathrm{SiC}\mathit{H}_2O$), 1.57 (234H, $C\mathit{H}_2CH_2CH_2Si$), 1.08 (234H, $CH_2C\mathit{H}_2CH_2Si$), 0.56 (234H, 18H, $CH_2CH_2C\mathit{H}_2Si$), 0.01 (702H, $\mathrm{Si}(C\mathit{H}_3)_2$). $^{13}$C NMR (1D 1H), ($CD_3CN$, 75 MHz): $\delta_{\mathrm{ppm}}$: 160.45 (arom. O*Cq*), 140.60 (*Cq* of arom.core), 138.77 (*Cq* of trz), 128.66 and 114.82 (arom. CH), 126.07 (CH of trz), 97.30 (*Cq* of Cp sub.), 87.10 (CH of Cp), 85.70, 81.89 (CH of Cp sub.), 61.67 ($CH_2OAr$), 44.31 ($CqCH_2CH_2CH_2Si$), 42.92 ($\mathit{Cq}CH_2CH_2CH_2Si$), 42.31 (trz-$CH_2Si$), 18.61 ($CqCH_2CH_2CH_2Si$), 15.74 ($CqCH_2CH_2CH_2Si$), −3.35 ($\mathrm{Si}(CH_3)_2$). $^{29}$Si NMR ($CD_3CN$, 79.5 MHz): $\delta_{\mathrm{ppm}}$: 0.46 (36 Si, *Si*$CH_2O$), 3.50 (81Si, *Si*$CH_2$trz). Anal. Calc. for $C_{1935}H_{2514}Si_{117}N_{243}Co_{81}O_{36}(PF_6)_{81}(H_2O)_5$: C 46.81, H 5.12; found: C 47.00 H 5.16.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

General data, detailed experimental procedures, spectroscopic data for compounds, NMR, and MALDI-TOF mass spectra, and CVs. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

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