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Click Chemistry of an Ethynylarene Iron Complex: Syntheses, Properties, and Redox Chemistry of Cationic Bimetallic and Dendritic Iron-Sandwich Complexes

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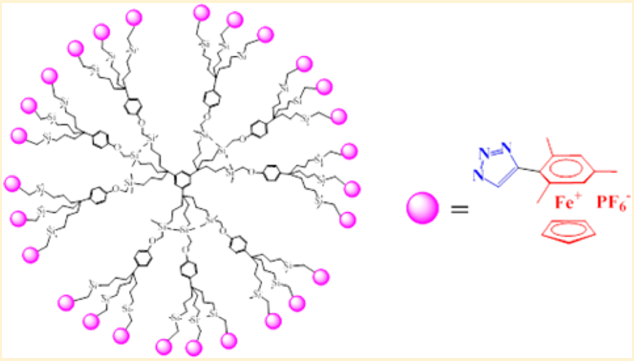
Supporting Information



ABSTRACT: The functionalization of dendrimers and other macromolecules with cationic redox-active organometallics remains a target toward metal-containing dendrimers and polymers that can serve in particular as polyelectrolytes and multielectron redox reagents. Along this line, we report the click functionalization of organometallics and dendrimers with a redox-active ethynylarene iron complex, $[\mathrm{FeCp}(\eta^6\text{-ethynylmesitylene})][\mathrm{PF_6}]$, **3**, easily available from $[\mathrm{FeCp}(\eta^6\text{-mesitylene})][\mathrm{PF_6}]$, **1**. Complex **3** reacts with azidomethylferrocene upon catalysis by copper sulfate and sodium ascorbate (CuAAC reaction) to give a bimetallic complex that is reduced on the mesitylene ligand to a mixture of isomeric cyclohexadienyl complexes. Complex **3** also reacts according to the same click reaction with zeroth- and first-generation metallodendrimers containing, respectively, 9 and 27 azido termini to provide new polar polycationic metallodendrimers that are reversibly reduced, on the electrochemical time scale, to 19-electron $\mathrm{Fe^I}$ species.

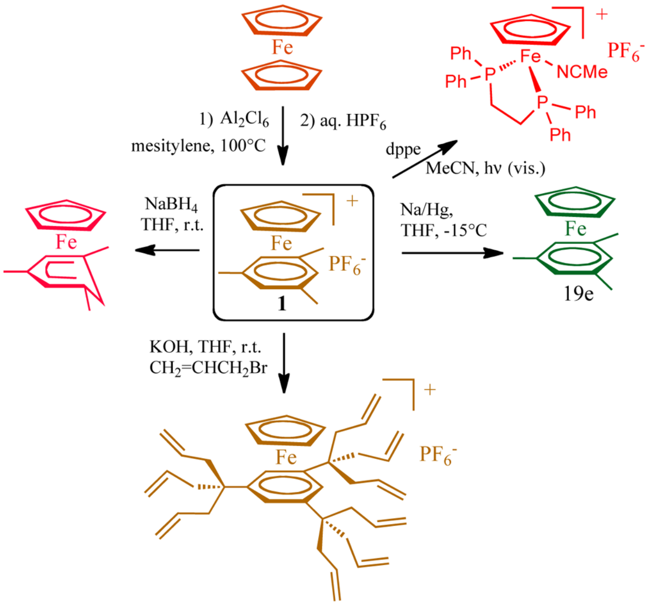
INTRODUCTION

Metallodendrimers are a rich chemistry[1] that finds applications in catalysis,[2] sensing,[3] molecular electronics,[4] and other molecular materials properties.[1] Metallocene-terminated dendrimers occupy a large part of this chemistry because of their rich redox properties that are especially developed and applied with ferrocene dendrimers.[5] Very few polycationic dendrimers are known, almost exclusively cobalticenium dendrimers,[6,7] however, despite their polyelectrolyte properties. The chemistry of the family of complexes $[\mathrm{FeCp}(\eta^6\text{-arene})][\mathrm{PF_6}]$[8] ($\mathrm{Cp} = \eta^5\text{-}\mathrm{C_5H_5}$) parallels that of cobalticenium[9] and is also quite rich. For instance, the basic properties of the readily available complex $[\mathrm{FeCp}(\eta^6\text{-mesitylene})][\mathrm{PF_6}]$, **1**,[10] are illustrated in Scheme 1. Further functionalization of **1** was thus a target in order to graft this cheap and easily available cationic and redox-active organoiron complex onto the periphery of dendrimers.

Recently, it has been possible to nearly quantitatively functionalize complex **1** by the introduction of an ethynyl group on the arene ligand upon addition of the ethynyl carbanion in the form of lithium acetylideethylenediamine in THF giving *exo*-cyclohexadienyl adduct **2**, followed by removal of the *endo* hydride using commercial trityl hexafluorophosphate providing the ethynyl-substituted arene complex $[\mathrm{FeCp}(\eta^6\text{-ethynylmesitylene})][\mathrm{PF_6}]$, **3** (Scheme 2).[11]

This procedure is an extension of the very useful analogous functionalization of cobalticenium.[12] Complex **3** that is readily obtained in this way serves in further functionalization. For instance, the new facile hydroamination of this complex **2** leads

Scheme 1. Basic Chemistry of Complex 1



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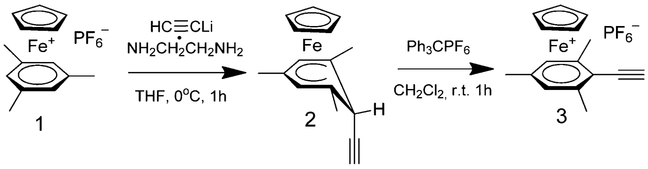
Scheme 2. Synthesis of Ethynyl Derivative 3



to the formation of conjugated *trans*-enamines,[11] but attempts to extend this functionalization to dendritic amines were unsuccessful, although such an extension worked well with ethynylcobalticenium.[13] However, we report here the successful and facile CuAAC click reaction[14] of **2** with azidomethylferrocene and dendritic azides yielding cationic bi- and polymetallic complexes of hexahapto-coordinated 1,2,3-triazolylmesitylene. The redox chemistry of these new cationic bimetallic and dendritic complexes is also detailed here.

■ RESULTS AND DISCUSSION

Click Reaction of Ethynylmesitylene Complex 3 with Azidomethylferrocene. The ethynyl derivative **3** of the complex $[FeCp(\eta^6\text{-}C_6H_3Me_3)]PF_6$, **1**, is synthesized according to the nucleophilic addition of lithium acetylideethylenediamine followed by hydride abstraction by $[Ph_3C][PF_6]$ (Scheme 2). (Azidomethyl)ferrocene **4** is then used in the CuAAC reaction with compound **3** to selectively produce 1,4-disubstituted triazolyl (trz) complex **5** in quantitative yield (Scheme 3).

The new dark-orange complex **5** is soluble in dichloromethane, THF, and chloroform and must be kept in the dark in the solid state in order to avoid its visible-light-induced photodecomplexation. The infrared spectroscopy shows the disappearance of the azido group at 2097 cm^{-1} and the appearance of the characteristic band of the PF_6^- anion at 839 cm^{-1}. The formation of the trz group is clearly shown in ^1H NMR spectroscopy by the appearance of the CH_2-trz and trz CH peaks at 5.55 and 8.41 ppm, respectively, and is also confirmed by the presence of the characteristic peaks of *Cq* and CH of trz in the ^{13}C NMR spectrum. Product **5** was additionally characterized by HMBC, HSQC, COSY, ^{31}P, and ^{19}F NMR spectroscopic techniques (Supporting Information). Finally, the structure of **5** was confirmed by the molecular peak at 506 Da in the mass spectrum corresponding to the positively charged complex **5** and by elemental analysis.

The cyclic voltammetry and redox chemistry of the iron-sandwich complexes including that of ferrocene[15] and of the family of $[FeCp(\eta^6\text{-arene})][PF_6]$ complexes[16] are well documented. The cyclic voltammograms (CVs) of complex **5** were recorded in DMF using decamethylferrocene as the internal reference[17] in order to investigate the redox properties of the triazolyl-$[Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})]PF_6$ group. The oxidation wave at 0.55 V vs $[FeCp^*_2]^{+/0}$ ($Cp^* = \eta^5\text{-}C_5Me_5$) is due to the oxidation of the ferrocenyl fragment to the 17-electron ferricenium species, and the reduction wave at −1.36 V vs $[FeCp^*_2]^{+/0}$ is due to the reduction of the triazolyl-$[Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})]PF_6$ fragment to its 19-electron Fe^I isostructural analogue.[8b] Both waves show electrochemical and chemical reversibility under N_2 indicating the robustness of compound **5** and the triazolyl group attached to the $[Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})]PF_6$ sandwich under these conditions. When the CV is recorded under air, the situation changes, however. The reduction wave of triazolyl-$[Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})]PF_6$ is then irreversible with a potential Ep of −1.34 V vs $[FeCp^*_2]^{+/0}$, whereas remarkably a new irreversible oxidation wave appeared at −0.68 V vs $[FeCp^*_2]^{+/0}$. It is known that the 19-electron complex $[Fe^{II}(\eta^5\text{-}Cp)(\eta^6\text{-}C_6Me_6)]$ is extremely reactive toward O_2, reacting with an overall H atom abstraction from a benzylic methyl substituent according to a mechanism that comprises electron transfer from Fe^I to O_2 followed by deprotonation by superoxide O_2^- giving the 18-electron cyclohexadienylidene-methylene complex $[Fe^{II}(\eta^5\text{-}Cp)(\eta^5\text{-}C_6Me_5CH_2)]$.[18] It seems that the 19-electron species triazolyl-$[Fe^I(\eta^5\text{-}Cp)(\eta^6\text{-}C_6H_2Me_3\text{-})]$ generated at the cathode by single-electron reduction of **5** reacts analogously with O_2 from air giving triazolyl-$[Fe^{II}(\eta^5\text{-}Cp)(\eta^5\text{-}C_6H_2Me_2CH_2\text{-})]$, although this cyclohexadienylidene-methylene species has not been isolated in this case. This reaction appears here to be faster than the electrochemical time scale as expected; thus, it probably is this oxidized species that is then oxidized at −0.68 V (Figure 1).

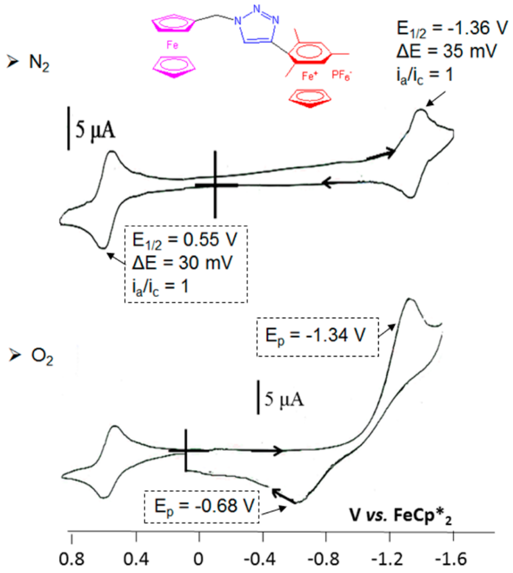
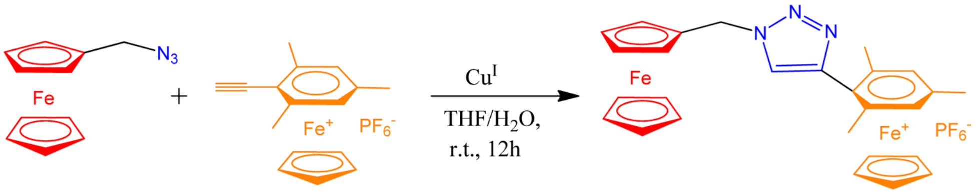
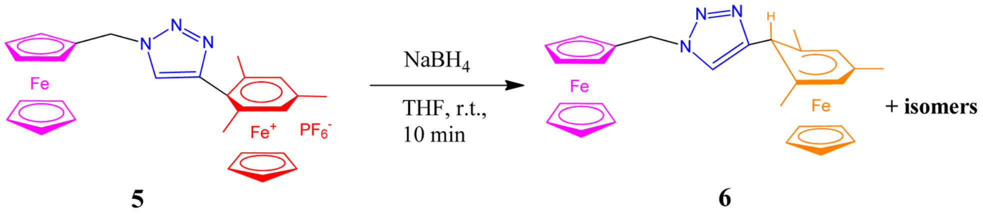


Figure 1. CVs of **5** under N_2 and under O_2 (air). Solvent, DMF; reference electrode, Ag; working and counter electrodes, Pt; scan rate, 0.2 V/s; and supporting electrolyte, $[n\text{-}Bu_4N][PF_6]$, 0.1M.

Scheme 3. "Click" Synthesis of Bimetallic Complex 5



Scheme 4. Reduction of the Complex Fc-CH_2-trz-Fe^{II}(η^5-Cp)(η^6-$C_6H_2Me_3$-)]PF_6, 5, (Fc = ferrocenyl) by $NaBH_4$ Giving Neutral Bimetallic Complex 6 and Isomers



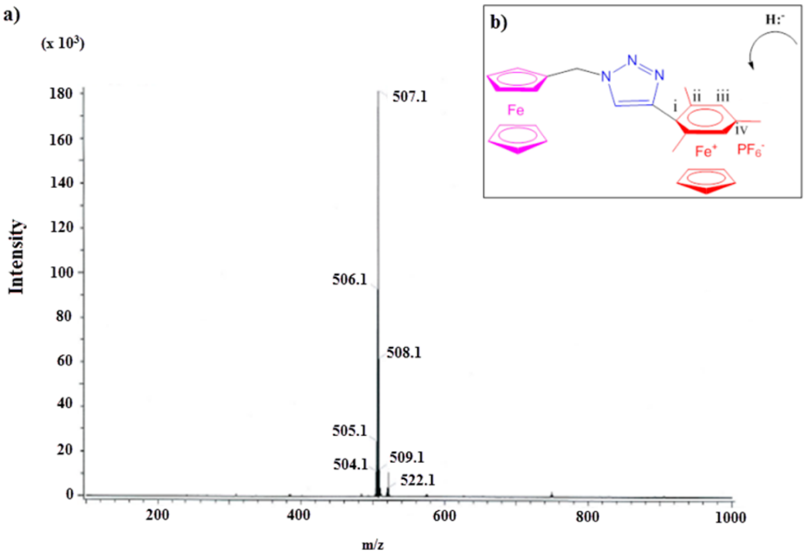


Figure 2. (a) FD-MS of neutral compound **6** and isomers and (b) possible hydride addition on four positions i, ii, iii, and iv of the mesitylene ligand (ii and iv are steroelectronically disfavored).

Reduction of Binuclear Triazole Complex 5 by $NaBH_4$. The complexes of the [FeCp(η^6-arene)][PF_6] family are known to be reducible by $NaBH_4$ on the arene ligand producing a decrease of hapticity to yield cyclohexadienyl complexes, and in the presence of methyl substituents on the arene ligand, the unsubstituted carbon atoms of the ligand are preferentially attacked.[19] In accord with this rule,[20] reduction of the dark-orange cationic complex **5** by $NaBH_4$ at 0 °C in THF produces the light-orange complex **6** that contains two iron-sandwich units with both pentahapto ligands. Complex **6** is soluble in less polar solvents such as diethyl ether, which allows its extraction under N_2 (Scheme 4). Compound **6** is air-sensitive but not light-sensitive, contrary to the complexes of the [Fe^{II}(η^5-Cp)(η^6-arene)]PF_6 family.[8b,21]

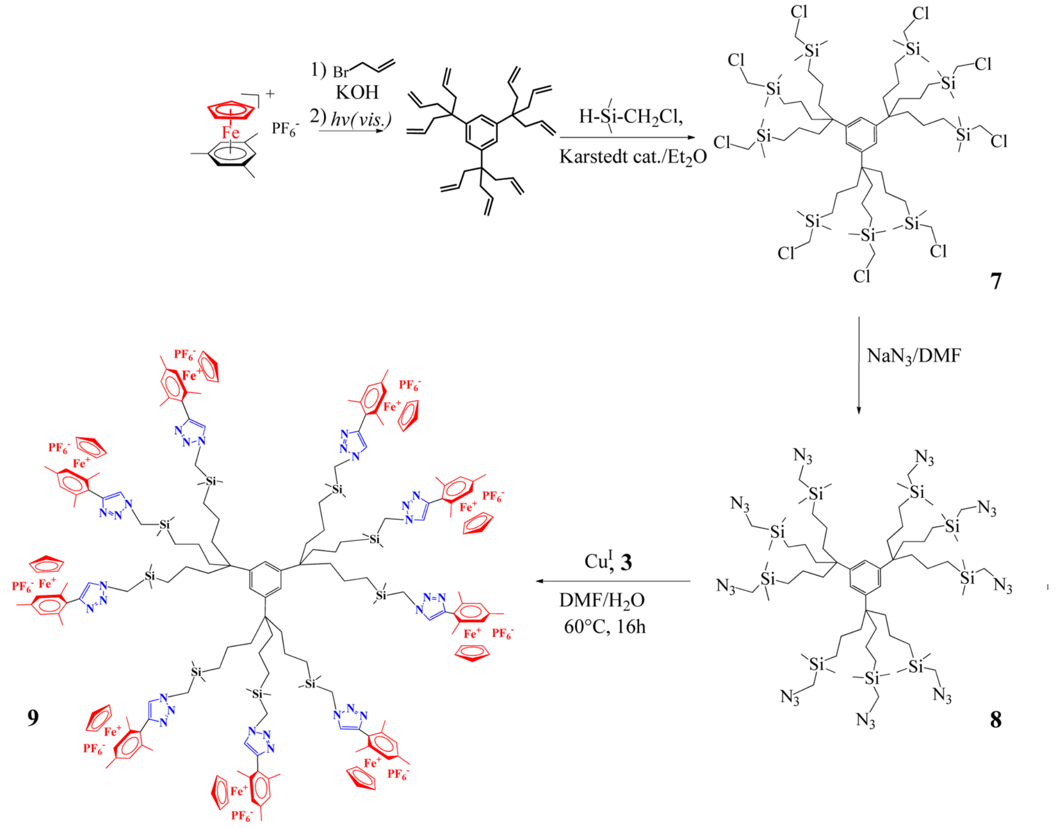
Compound **6** together with isomers have been isolated in 80% yield, and their structure is confirmed by the observation of the molecular peak in the FD-mass spectrum (Figure 2a). Compound and isomers **6** have been further characterized by ^{1}H NMR, ^{13}C NMR, and HSQC spectroscopy, which is rather complex, showing the formation of a mixture of isomers corresponding to different positions of the hydride addition. The same phenomenon has been observed for the reduction of triazolyl-cobalticenium complexes by $NaBH_4$.[22] Indeed the hydride reduction of compound **5** might occur on positions i, ii, iii, and iv of the mesitylene ligand (preferentially in i and iii due to sterically and electronically disfavored hydride attack on the methyl-substituted arene carbon atoms) as indicated in Figure 2b. In all cases, the hydride is located in *exo* position on the mesitylene ligand as a result of the *exo* hydride attack. No attempt was made to identify and separate the isomers.

The cyclic voltammogram in THF shows a totally irreversible oxidation wave at 0.20 V vs. [$FeCp_2$*]$^{+/0}$. It is suggested that this wave corresponds to the oxidation of the compound **6** and its isomers (Supporting Information). This wave is very large, representing the subsequent irreversible oxidation of **6** and its isomers back to the starting material, complex **5**.

Grafting [FeCp(η^6-ethynylmesitylene)][PF_6] onto Dendrimers by Click Chemistry. Grafting [FeCp(η^6-ethynylmesitylene)][PF_6] on macromolecules was a challenge because of several factors. First, the visible-light sensitivity of the complexes of the [FeCp(η^6-arene)][PF_6] family and more particularly of the click reaction products because of the electron-withdrawing trz substituent[21] leads to a rapid decoordination of the mesitylene ligand. Then, an additional difficulty is the solubility problem that reduces the choice of solvent, while coordinating solvents are not permitted because of ligand displacement due to the cationic electron-poor arene ligand bond in **3**. Finally, the steric effect of the *ortho*-methyl groups that had most probably been responsible for the lack of success of the extension of the useful hydroamination to dendritic amines might also cause failure of the click reaction. Finally, however, click chemistry has proved to be an efficient way for the incorporation of **3** into dendrimers, and the CuAAC reaction has been successfully conducted between **3** and polyazido-terminated dendritic precursors for the synthesis of the cationic metallodendrimers.

The synthesis of the polyazido dendrimers begins with the synthesis of arene-centered dendrimers according to the classic CpFe$^+$-induced nona-allylation of mesitylene in [FeCp(η^6-1,3,5-$C_6H_3(CH_3)_3$)][PF_6][23] according to the 1 → 3 con-

Scheme 5. Synthesis of the Dendrimer G$_0$-Nona-[Fe^{II}(η^5-Cp)(η^6-C$_6$H$_2$Me$_3$-)]PF$_6$, 9



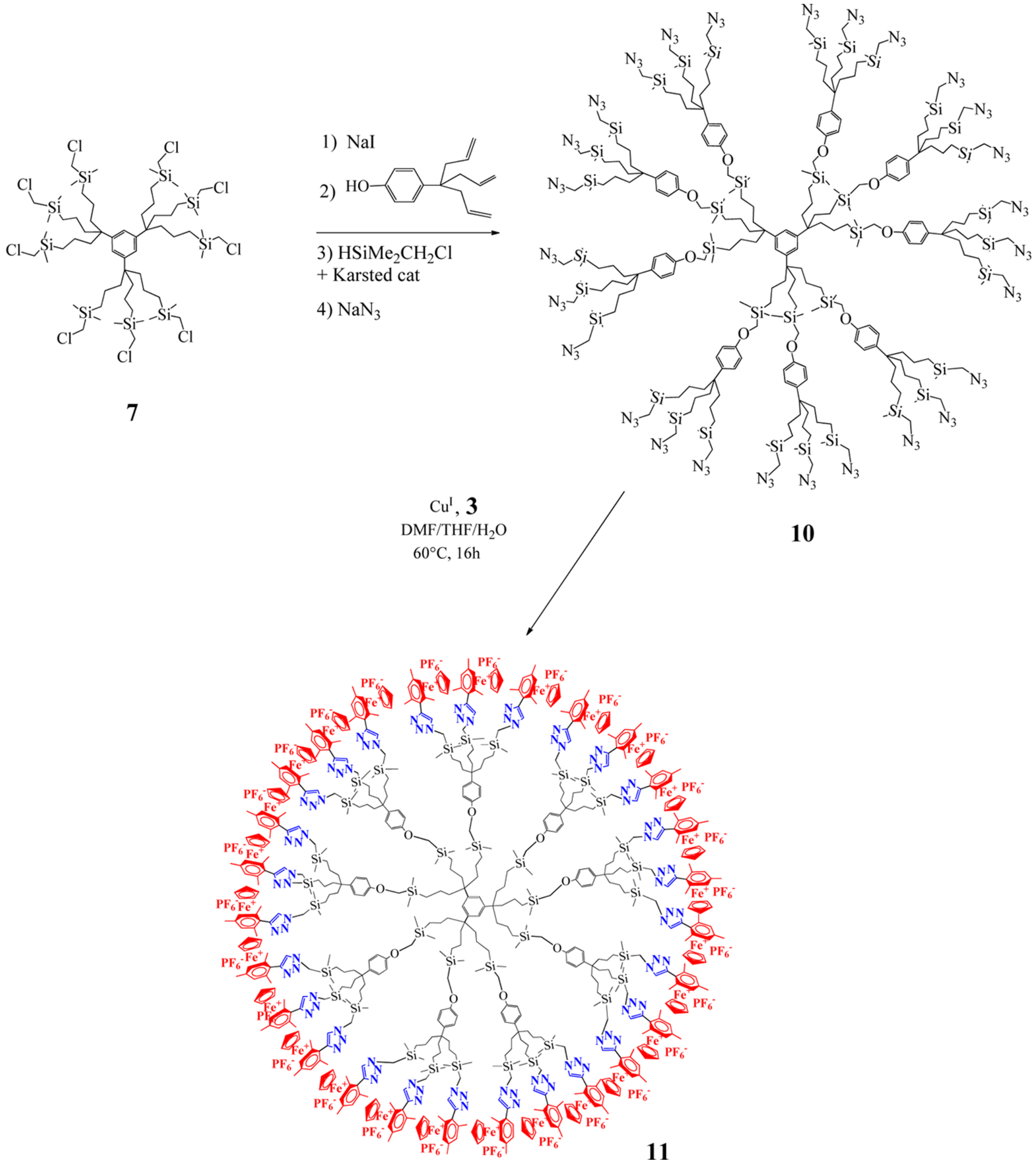
nectivity pioneered by Newkome.[24] This reaction provides the nonaallyl core and is followed by hydrosilylation with chloromethyldimethylsilane[25] and substitution of the terminal chloro group in **7** by reaction with sodium azide giving the zeroth-generation dendritic nonaazide **8**. The following dendrimer generation containing 27 terminal allyl groups is obtained by Williamson reaction of the nona-chloro core **7** with a phenol triallyl dendron[23] according to a known procedure.[23b] It is followed by substitution of the terminal chloride by the azido group by reaction with NaN$_3$. This sequence of reactions provides the known first-generation dendrimer **10** containing 27 N$_3$ termini.[26]

Click reactions follow between these dendritic azido precursors and alkyne **3**. The solvents in each reaction are chosen in order to achieve the solubility of the final product because the polycationic poly-[Fe^{II}Cp(η^6-C$_6$H$_2$Me$_3$-)]PF$_6$ dendrimers are soluble only in high polarity solvents. For the synthesis of the dendrimer, G$_0$-nona-[Fe^{II}Cp(η^6-C$_6$H$_2$Me$_3$-)]-PF$_6$, **9**, DMF/H$_2$O 4:1 is chosen as solvent, whereas for the dendrimer of higher generation G$_1$-27-[Fe^{II}(η^5-Cp)(η^6-C$_6$H$_2$Me$_3$-)]PF$_6$, **11**, a mixture of DMF/THF/H$_2$O is used because the azido-terminated precursor **10** is insoluble in DMF. The temperature of the reactions is maintained at 60 °C, and the reaction mixtures are left stirring during 16 h. The copper salt is finally removed as [Cu(NH$_3$)$_2$(H$_2$O)$_2$] [SO$_4$] by adding an aqueous solution of NH$_3$ that is left stirring with the mixture for 15 min. The resulting dendrimers **9** (Scheme 5) and **11** (Scheme 6) are purified, after workup in the dark, by precipitation in diethyl ether as yellowish powders. Washing with the less polar THF solvent in which they are insoluble permits one to separate the excess of starting material **3** and further impurities to finally give products **9** and **11** that are fully characterized by ^{1}H, ^{13}C, ^{19}F, ^{31} P, HMBC, HSQC, COSY NMR, IR, cyclic voltammetry, and elemental analysis. MALDI-TOF analysis is also attempted for the smaller dendrimer **9** for which the molecular peak is observed even though the mass spectrum is an ensemble of multiple fragments due to the high instability of the dendrimer under these conditions (see Supporting Information).

Indeed, dendrimers **9** and **11** are very polar because the fragment trz-[Fe^{II}(η^5-Cp)(η^6-C$_6$H$_2$Me$_3$-)]PF$_6$ is very hydrophilic and soluble only in very polar solvents. Particularly, dendrimers **9** and **11** can be dissolved in acetone, acetonitrile, methanol, and DMF. However, these dendrimers are not soluble in water despite the presence of several cationic organometallic fragments at their periphery. Another observation is that dendrimers **9** and **11** are not stable in acetonitrile solution because acetonitrile is a competing ligand with mesitylene for coordination to iron(II), and precipitation occurs after several hours. Furthermore, exposure of these dendrimers to ambient light in solution or in the solid state also leads to rapid decomplexation of the mesitylene ligand. When kept in the dark, however, dendrimers **9** and **11** are stable compounds.

Infrared spectroscopy is a very useful tool to monitor the click reactions with dendrimers because the characteristic peak of the azido groups at about 2094 cm^{-1} disappears at the end of the reactions confirming their replacement by the 1,2,3-triazole groups. The characteristic absorption of the PF$_6^-$ anion of these PF$_6^-$ salts shows a strong band in the range 836−842 cm^{-1}. The absorptions due to the =C−H stretching of the triazole and Cp groups of the trz-[Fe^{II}(η^5-Cp)(η^6-C$_6$H$_2$Me$_3$-)]PF$_6$ unit are found in the range 3095−3127 cm^{-1}.

Scheme 6. Synthesis of G_1-27-[$Fe^{II}(\eta^5$-Cp)(η^6-$C_6H_2Me_3$-)]PF_6 Dendrimer 11



NMR spectroscopy confirms the structure of the trz-[$Fe^{II}(\eta^5$-Cp)(η^6-$C_6H_2Me_3$-)]PF_6 products. Particularly, in ^{1}H NMR the formation of the trz ring is clearly shown by the appearance of the peaks around 8.27 ppm (in CD_3OD or CD_3COCD_3) for the products **9** and **11**. In both cases, the peak of SiCH_2-N_3 at 2.7−2.8 ppm disappears, whereas the appearance of the new peak of SiCH_2-trz takes place at about 4.2 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 $SiCH_2$-trz in the ^{13}C NMR spectra. Finally, the assignments of the number of protons in ^{1}H NMR show the expected ratio between the dendritic frame part and the trz-[$Fe^{II}(\eta^5$-Cp)(η^6-$C_6H_2Me_3$-)]-PF_6 groups. The ^{19}F and ^{31}P NMR spectra show the characteristic peaks of the PF_6^- counteranion. 2-D NMR data (HSQC, HMBC, and COSY) show the correct correlation between proton/proton and proton/carbon peaks. Finally, elemental analysis confirms the structure of the dendrimers **9** and **11**.

Cyclic Voltammetry of the Cationic Metallodendrimers 9 and 11. Both dendrimers **9** and **11** are also studied by cyclic voltammetry using decamethylferrocene as the internal reference,[17] in DMF, a good solubility being accessible with this solvent. Different conditions such as temperature and air (O_2)/N_2 atmosphere are examined. A cathodic CV wave in all the products is observed around −1.34 V vs $[FeCp^*_2]^{0/+}$ and corresponds to the reduction of [Fe^{II}Cp(η^6-$C_6H_2Me_3$-)]-PF_6 to the 19-electron species [Fe^{I}Cp(η^6-$C_6H_2Me_3$-)]. In all cases, this wave is single in DMF, which is explained by the

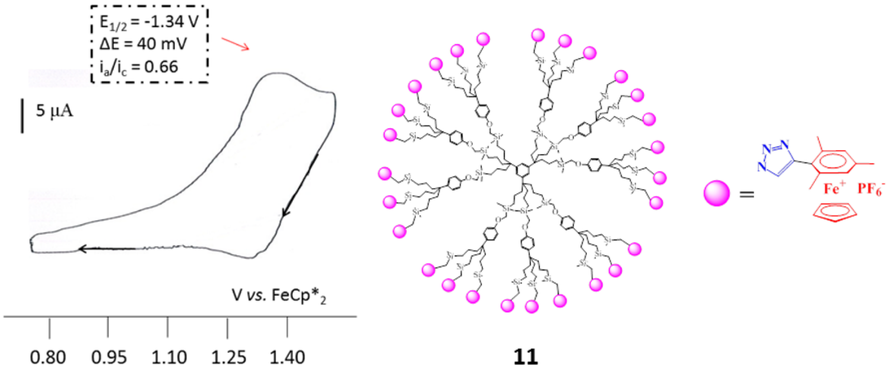


Figure 3. CV of dendrimer **11** in DMF under N_2. Internal reference, FeCp*$_2$; reference electrode, Ag; working and counter electrodes, Pt; scan rate, 0.2 V/s; supporting electrolyte, [*n*-Bu$_4$N][PF$_6$].

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.[27] However, the envelope of the redox wave is broad, which is presumably due to electrostatic interactions differentiating the various single electron-transfer steps.

When recording the CVs of dendrimers **9** and **11** under aerobic (O_2) atmosphere, the same phenomenon as that for compound **5** is observed. The reduction wave of the fragments $[Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})]PF_6$ is irreversible due to the fast reaction of the 19-electron species with O_2 (vide supra). However, when the electrochemical experiments are performed under nitrogen at room temperature, the cathodic wave ($Fe^{II/I}$) becomes chemically and electrochemically reversible. The peak-to-peak potential difference between the cathodic and anodic waves is 30−40 mV, significantly narrower compared with the Nernstian one-electron process, probably due to some adsorption onto the electrode. The electrochemical reversibility involving equally all of the redox groups is due to very fast rotation within the electrochemical time scale because all of the redox groups come close to the electrode, provoking fast electron transfer between these groups and the electrode,[28] and/or the electron-hopping mechanism.[29] The CV wave under N_2 of dendrimer **11** containing 27 $[Fe^{II}(\eta^5\text{-}Cp)(\eta^6\text{-}C_6H_2Me_3\text{-})]PF_6$ termini is shown in Figure 3.

CONCLUDING REMARKS

The currently used click reaction, i.e., the Huisgen-type CuAAC, proves to be most useful to graft organometallic complexes onto the periphery of dendrimers.[30] Here, the newly functionalized, easily available complex **3** is a remarkable illustration insofar as the hydroamination of **3** could not provide such iron-sandwich terminated dendrimers. In spite of their sensivity to visible light and coordinating solvents such as acetonitrile, the polycationic metallodendrimers were fully characterized. The electron-withdrawing 1,2,3-triazolyl linkage formed by the CuAAC reaction does not significantly perturb the chemical and electrochemical reversibility of the cathodic reduction to the Fe^I 19-electron species at least during the electrochemical time scale under an inert atmosphere. This chemistry adds to the versatility of the functionalization and redox properties of the family of $[FeCp(\eta^6\text{-arene})][PF_6]$ complexes that parallels the cobalticenium family and opens the route to new cationic metallodendrimers and metal-containing macromolecules and polyelectrolytes.

EXPERIMENTAL SECTION

General Data. Reagent-grade tetrahydrofuran (THF) was predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. All other solvents and chemicals were used as received. The ^1H NMR spectra were recorded at 25 °C with a Bruker AVANCE II 400 MHz spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 100 MHz with a Bruker AVANCE 400 spectrometer. ^{19}F NMR spectra were recorded at 25 °C in a 376 MHz with a Bruker AVANCE II 400 MHz spectrometer. ^{31}P NMR was recorded at 25 °C at 162 MHz with a Bruker AVANCE II 400 MHz spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS). The infrared (IR) spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. The results of elemental analysis were obtained by a Thermo Flash 2000 EA. The sample was introduced in a tin container for NCHS analysis and in a silver container for oxygen analysis. The mass spectra were performed by the CESAMO (Bordeaux, France) on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source, and spectra were recorded in the positive mode. The electrospray needle was maintained at 5000 V and operated at room temperature. Samples were introduced by injection through a 20 μL sample loop into a 4500 μL/min flow of methanol from the LC pump. The mass spectrum of compound **6** was obtained by the CESAMO on a AccuTOF-GcV (JEOL), which is a GC-TOF. The instrument is equipped with a sample introduction system named FD (Field Desorption). The MALDI-TOF mass spectra were obtained by the CESAMO (Bordeaux, France) on a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. All electrochemical measurements (CV) were recorded under the following conditions: solvent, dry DMF; temperature, 20 °C; supporting electrolyte, [*n*Bu$_4$N][PF$_6$] 0.1M; working and counter electrodes, Pt; reference electrode, Ag; internal reference, FeCp*$_2$; scan rate, 0.200 V·s^{-1}.

Complex 5. A mixture of 1 equiv of azidomethylferrocene (60 mg, 0.23 mmol) and 1 equiv of ethynyl compound **3** (94 mg, 0.23 mmol) were dissolved in 3/2 distilled THF/H_2O. At 0 °C, $CuSO_4$ was added (1 equiv; 1 M aqueous solution), followed by dropwise addition of a freshly prepared solution of sodium ascorbate (2 equiv; 1 M aqueous solution). The solution was allowed to stir for 12 h at r.t. under N_2. Then, an aqueous solution of ammonia was added, and the mixture was allowed to stir for 10 min. The organic phase was washed twice with water, dried with sodium sulfate, and filtered through paper, and the solvent was removed *in vacuo*. Complex **5** was purified by precipitation with diethyl ether and obtained as dark-orange powder in quantitative yield (154 mg). ^1H NMR of **5** (CD_3COCD_3, 400 MHz), δ_{ppm}: 8.41 (1H, C*H* of trz), 6.43 (2H, C*H* of mesitylene), 5.55 (2H of trz−CH_2), 5.17 (5H, C*H* of Cp of $[Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})]PF_6$, 4.45 (2H, C*H* of Cp sub. of $FeCp_2$), 4.25 (2H, C*H* of Cp sub. and 5H, C*H* of Cp free of $FeCp_2$), 2.56 (3H, −CHCCH_3) and 2.35 (6H, trzCCCH_3). ^{13}C NMR of **5** (CD_3COCD_3, 100 MHz), δ_{ppm}: 139.88 (*Cq* of trz), 125.86 (CH of trz), 102.80 (trz-*Cq*), 102.75 (trz-C*Cq*), 94.44 (CH*Cq* of mesitylene), 88.48 (CH of mesitylene), 82.50 (*Cq* of Cp sub. of $FeCp_2$), 78.78 (CH of Cp of -[$Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})$]$PF_6$, 69.01 (CH of Cp of $FeCp_2$), 68.93 and 68.88 (CH of Cp sub. of $FeCp_2$), 50.08 (trz-CH_2), 19.61 and 19.54 (−CH_3 of mesitylene). ^{19}F NMR of **5** (CD_3COCD_3, 376 MHz), δ_{ppm}: doublet centered at −73.3 ppm ($J_{F\text{-}P}$ = 710 Hz). ^{31}P NMR of **5** (CD_3COCD_3, 162 MHz), δ_{ppm}: −144.1 ppm (hept., PF_6^-) ($J_{P\text{-}F}$ = 710 Hz). ESI MS of **5** (*m*/*z*): Calcd for $C_{27}H_{28}N_3Fe_2^+$, 506.097 Da; found, 506.098 Da. Anal. Calcd for $C_{27}H_{28}N_3Fe_2PF_6$: C, 49.80; H, 4.33. Found C, 50.10; H, 4.51.

Complex 6. A mixture of 1 equiv of **5** (30 mg, 0.046 mmol) with 2 equiv of $NaBH_4$ (1.7 mg, 0.092 mmol) in 20 mL of distilled THF was stirred for 10 min under N_2. Then, the solvent was evaporated *in vacuo*, and distilled diethyl ether was added to solubilize the neutral product. After filtration under N_2 and evaporation of the solvent *in vacuo*, the product was obtained as a light-orange powder. Yield: 80% (19 mg). Complex **6** is not stable in air and was stored under N_2. ^1H NMR of **6** ($CDCl_3$, 400 MHz), δ_{ppm}: 7.88−7.11 (1H, C*H* of trz), 6.36−6.06 (C*H* of mesitylene), 5.42−5.25 (2H of trz−$C\mathit{H}_2$ and H of diene), 4.93−4.00 (5H, C*H* of Cp of [$Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})$]$PF_6$ and (9H, C*H* of Cp of $FeCp_2$), 2.46−2.20 and 1.40−1.17 (9H, $-C\mathit{H}_3$), 1.90−1.64 (H in exo position). ^{13}C NMR of **6** ($CDCl_3$, 100 MHz), δ_{ppm}: 137.65 (Cq of trz), 123.20 (CH of trz), 102.31 (trz-*Cq*), 98.71 (trz-C*Cq*), 94.60 (CH*Cq* of mesitylene), 88.33 (CH of mesitylene), 79.56 (*Cq* of Cp sub. of $FeCp_2$), 79.56−75.04 (CH of Cp of -[$Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})$]$PF_6$, 69.48−68.78 (CH of $FeCp_2$), 49.93 (trz-CH_2), 39.74, 39.00 and 30,02 (CH exo), 25.65−19.96 (−CH_3 of mesitylene). MS (*m*/*z*) of **6**: Calcd for $C_{27}H_{29}Fe_2N_3$, 507.1060; found, 507.1055.

Compound 9. Azido-terminated dendrimer **8** (1 equiv, 30 mg, 0.020 mmol) and complex **3** (13.5 equiv., 110.7 mg, 0.27 mmol) were dissolved in 20 mL of anhydrous and degassed DMF, then 3 mL of degassed water was added, and the reaction mixture was cooled to 0 °C. Then, an aqueous solution of 1 M $CuSO_4$ (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 yellow to dark orange 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 evaporated *in vacuo*, 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 in order to remove all of the copper salt trapped inside the dendrimer. The organic phase was washed twice with water, dried over sodium sulfate, and filtered, and the solvent was removed *in vacuo*. Then, the product was precipitated from an acetone solution in diethyl ether and washed with THF to remove the excess of alkyne and further impurities. Product **9** was obtained as an orange-yellow powder. Yield: 65% (67 mg). ^1H NMR of **9** (CD_3OD, 400 MHz): δ_{ppm}: 8.23 (9H, C*H* of trz), 7.18 (3H, C*H* of arom.core), 6.33 (18H, C*H* of mesitylene), 5.03 (45H, C*H* of Cp of [$Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})$]$PF_6$, 4.16 (18H, $SiC\mathit{H}_2$-trz), 2.48 (27H, $-CHCC\mathit{H}_3$), 2.25 (54H, $trzCCC\mathit{H}_3$) 1.80 (18H, $C\mathit{H}_2CH_2CH_2Si$), 1.31 (18H, $CH_2C\mathit{H}_2CH_2Si$), 0.76 (18H, $CH_2CH_2C\mathit{H}_2Si$), 0.13 (54H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR of **9** (CD_3OD, 100 MHz), δ_{ppm}: 145.09 (*Cq* of arom.core), 138.24 (*Cq* of trz), 127.12 (CH of trz), 124.41 (CH of arom.core), 102.46 (trz-Cq and trz-C*Cq*), 94.05 (CH*Cq* of mesitylene), 88.34 (CH of mesitylene), 78.37 (CH of Cp of [$Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})$]$PF_6$, 44.00 ($CqCH_2CH_2CH_2Si$), 42.01 ($\mathit{Cq}CH_2CH_2CH_2Si$), 40.72 (trz-$CH_2Si$), 20.34 and 20.20 (−$CH_3$ of mesitylene), 17.91 ($CqCH_2CH_2CH_2Si$), 14.92 ($CqCH_2CH_2CH_2Si$), −4.61 ($Si(CH_3)_2$). ^{19}F NMR of **9** (CD_3OD, 376 MHz), δ_{ppm}: doublet centered at 75.3 ppm ($J_{F\text{-}P}$ = 710 Hz). Anal. Calcd for $C_{207}H_{282}Si_9N_{27}Fe_9P_9F_{54}(H_2O)$: C 47.57, H 5.48; found, C 47.64 H 5.22.

Compound 11. Azido-terminated dendrimer **10** (1 equiv, 22.5 mg, 0.004 mmol) and complex **3** (40.0 equiv, 60 mg, 0.144 mmol) were dissolved in a mixture of 20 mL of anhydrous and degassed DMF and 15 mL of anhydrous and degassed THF, then 3 mL of degassed water was added, and the reaction mixture was cooled to 0 °C. Then, an aqueous solution of 1 M $CuSO_4$ (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 yellow to dark orange 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 evaporated *in vacuo*, 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 in order to remove all the copper salt trapped inside the dendrimer. The organic phase was washed twice with water, dried over sodium sulfate, and filtered, and the solvent was removed *in vacuo*. Then, the product was precipitated from an acetone solution in diethyl ether and washed with THF to remove the excess of alkyne and further impurities. Product **11** was obtained as an orange-yelow powder. Yield: 56% (35 mg). ^1H NMR of **11** (CD_3COCD_3, 400 MHz), δ_{ppm}: 8.32 (27H, C*H* of trz), 7.30, 6.90 (39H, C*H* of arom.core), 6.42 (54H, C*H* of mesitylene), 5.12 (135H, C*H* of Cp of [$Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})$]$PF_6$, 4.20 (54H, $SiC\mathit{H}_2$-trz), 3.59 (18H, $SiC\mathit{H}_2O$), 2.51 (3H, $-CHCC\mathit{H}_3$) and 2.31 (6H, $trzCCC\mathit{H}_3$), 1.73 (72H, $C\mathit{H}_2CH_2CH_2Si$), 1.28 (72H, $CH_2C\mathit{H}_2CH_2Si$), 0.71 (72H, $CH_2CH_2C\mathit{H}_2Si$), 0.10 (216H, $Si(C\mathit{H}_3)_2$). ^{13}C NMR of **11** (CD_3COCD_3, 100 MHz), δ_{ppm}: 159.58 (arom. O*Cq*), 139.66 (*Cq* of trz), 137.47 (*Cq* of arom.core), 127.51 and 113.81 (arom. CH), 125.59 (CH of trz), 102.76 (trz-*Cq*), 102.67 (trz-C*Cq*), 94.58 (CH*Cq* of mesitylene), 88.53 (CH of mesitylene), 78.78 (CH of Cp of [$Fe^{II}Cp(\eta^6\text{-}C_6H_2Me_3\text{-})$]$PF_6$, 60.20 ($CH_2OAr$), 43.25 ($CqCH_2CH_2CH_2Si$), 42.21 ($\mathit{Cq}CH_2CH_2CH_2Si$), 40.97 (trz-$CH_2Si$), 19.61 (−$CH_3$ of mesitylene), 17.70 ($CqCH_2CH_2CH_2Si$), 14.82 ($CqCH_2CH_2CH_2Si$), −4.16 ($Si(CH_3)_2$). ^{19}F NMR of **11** (CD_3COCD_3, 376 MHz), δ_{ppm}: doublet centered at 73.3 ppm ($J_{F\text{-}P}$ = 710 Hz). ^{31}P NMR of **11** (CD_3COCD_3, 162 MHz), δ_{ppm}: −144.1 ppm (hept., PF_6^-) ($J_{P\text{-}F}$ = 710 Hz). Anal. Calcd for $C_{720}H_{975}Si_{36}N_{81}Fe_{27}O_9(PF_6)_{27}(H_2O)_2$: C 49.76, H 5.68; found, C 49.48 H 5.81.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data for the bimetallic and metallodendritic complexes (IR, NMR, and mass spectra) and cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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