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, [FeCp(η⁶-ethynylmesitylene)][PF₆], 3, easily available from [FeCp(η⁶-mesitylene)][PF₆], 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 Fe⁺ species.

INTRODUCTION

Metallodendrimers are a rich chemistry¹ that finds applications in catalysis,² sensing,³ molecular electronics,⁴ and other molecular materials properties.¹ Metalloocene-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 [FeCp(η⁶-arene)][PF₆]³⁹ (Cp = η⁵-C₅H₅) parallels that of cobalticenium⁹ and is also quite rich. For instance, the basic properties of the readily available complex [FeCp(η⁶-mesitylene)][PF₆], 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 [FeCp(η⁶-ethynylmesitylene)][PF₆], 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...
to the formation of conjugated trans-enamines,\textsuperscript{14} but attempts to extend this functionalization to dendritic amines were unsuccessful, although such an extension worked well with ethynylcobaltincium.\textsuperscript{13} However, we report here the successful and facile CuAAC click reaction\textsuperscript{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.

\section*{RESULTS AND DISCUSSION}

**Click Reaction of Ethynylmesitylene Complex 3 with Azidomethylferrocene.** The ethynyl derivative 3 of the complex [FeCp(\(\eta^5\)-C\(_6\)H\(_2\)Me\(_3\)])PF\(_6\), 1, is synthesized according to the nucleophilic addition of lithium acetylideethylenediamine followed by hydride abstraction by [Ph\(_3\)C][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 \(^1\)H 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\textsuperscript{15} and of the family of [FeCp(\(\eta^5\)-arene)][PF\(_6\)] complexes\textsuperscript{16} are well documented. The cyclic voltammograms (CVs) of complex 5 were recorded in DMF using decamethylferrocene as the internal reference\textsuperscript{17} in order to investigate the redox properties of the triazolyl-[Fe\(_6\)Cp(\(\eta^5\)-C\(_6\)H\(_2\)Me\(_3\)])PF\(_6\) group. The oxidation wave at 0.55 V vs [FeCp\(_2^*\)]\(^{18}\) (Cp\(_\alpha^* = \eta^5\)-C\(_5\)Me\(_3\)) 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\(_2^*\)]\(^{18}\) is due to the reduction of the triazolyl-[Fe\(_6\)Cp(\(\eta^5\)-C\(_6\)H\(_2\)Me\(_3\)])PF\(_6\) fragment to its 19-electron Fe\(_\alpha^*\) isostructural analogue. Both waves show electrochemical and chemical reversibility under N\(_2\) indicating the robustness of compound 5 and the triazolyl group attached to the [Fe\(_6\)Cp(\(\eta^5\)-C\(_6\)H\(_2\)Me\(_3\)])PF\(_6\) sandwich under these conditions. When the CV is recorded under air, the situation changes, however. The reduction wave of triazolyl-[Fe\(_6\)Cp(\(\eta^5\)-C\(_6\)H\(_2\)Me\(_3\)])PF\(_6\) is then irreversible with a potential \(E_p\) of \(-1.34\) V vs [FeCp\(_2^*\)]\(^{18}\), whereas remarkably a new irreversible oxidation wave appeared at \(-0.68\) V vs [FeCp\(_2^*\)]\(^{18}\). It is known that the 19-electron complex [Fe\(_6\)(\(\eta^5\)-Cp)(\(\eta^5\)-C\(_5\)Me\(_3\)])\(^{18}\) is extremely reactive toward O\(_2\) reacring with an overall H atom abstraction from a benzylic methyl substituent according to a mechanism that comprises electron transfer from Fe\(_\alpha^*\) to O\(_2\) followed by deprotonation by superoxide O\(_2^−\) giving the 18-electron cyclohexadienylidene-methylene complex [Fe\(_6\)(\(\eta^5\)-Cp)(\(\eta^5\)-C\(_5\)Me\(_3\)])\(^{18}\). It seems that the 19-electron species triazolyl-[Fe\(_6\)(\(\eta^5\)-Cp)(\(\eta^5\)-C\(_5\)Me\(_3\)]) generated at the cathode by single-electron reduction of 5 reacts analogously with O\(_2\) from air giving triazolyl-[Fe\(_6\)(\(\eta^5\)-Cp)(\(\eta^5\)-C\(_5\)Me\(_3\)])\(^{18}\), 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).

![Scheme 2. Synthesis of Ethynyl Derivative 3](image)

**Scheme 2. Synthesis of Ethynyl Derivative 3**

![Scheme 3. “Click” Synthesis of Bimetallic Complex 5](image)

**Scheme 3. “Click” Synthesis of Bimetallic Complex 5**

![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, \([n-Bu_4N][PF_6]\), 0.1M.](image)
Reduction of Binuclear Triazole Complex 5 by NaBH₄. The complexes of the \([\text{FeCp}(\text{η}^6-\text{arene})][\text{PF}_6]\) family are known to be reducible by NaBH₄ 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.²⁰ In accord with this rule,²¹ reduction of the dark-orange cationic complex 5 by NaBH₄ 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 N₂ (Scheme 4). Compound 6 is air-sensitive but not light-sensitive, contrary to the complexes of the \([\text{Fe II}(\text{η}^5-\text{Cp})(\text{η}^6-\text{arene})][\text{PF}_6]\) family.²,²² Compound 6 together with isomers has 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 ¹H NMR, ¹³C 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 NaBH₄.²² 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.

Grafting \([\text{FeCp}(\text{η}^6-\text{ethynylmesitylene})][\text{PF}_6]\) onto Dendrimers by Click Chemistry. Grafting \([\text{FeCp}(\text{η}^6-\text{ethynylmesitylene})][\text{PF}_6]\) on macromolecules was a challenge because of several factors. First, the visible-light sensitivity of the complexes of the \([\text{FeCp}(\text{η}^6-\text{arene})][\text{PF}_6]\) family and more particularly of the click reaction products because of the electron-withdrawing trz substituent 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 polyazidoterminated 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 \([\text{FeCp}(\text{η}^6-1,3,5-\text{C}_6\text{H}_3(\text{CH}_3)_3)][\text{PF}_6]^{23}\) according to the \(1 \rightarrow 3\) con-
nectivity pioneered by Newkome. This reaction provides the nonaallyl core and is followed by hydrosilylation with chloromethylidimethylsilane 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 according to a known procedure. It is followed by substitution of the terminal chloride by the azido group by reaction with NaN₃. This sequence of reactions provides the known first-generation dendrimer containing 27 N₃ termini. 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-[FeII(η⁵-Cp)(η⁶-C₆H₂Me₃-)]PF₆ dendrimers are soluble only in high polarity solvents. For the synthesis of the dendrimer, G₀-nona-[FeIII(η⁶-C₆H₂Me₃-)]PF₆, DMF/H₂O 4:1 is chosen as solvent, whereas for the dendrimer of higher generation G₁-27-[FeII(η⁶-C₆H₂Me₃-)]PF₆, a mixture of DMF/THF/H₂O is used because the azido-terminated precursor 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(NH₃)₂(H₂O)] [SO₄] by adding an aqueous solution of NH₃ that is left stirring with the mixture for 15 min. The resulting dendrimers (Scheme 5) and (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 and further impurities to finally give products and that are fully characterized by ¹H, ¹³C, ¹⁹F, ³¹P, HMBC, HSQC, COSY NMR, IR, cyclic voltammetry, and elemental analysis. MALDI-TOF analysis is also attempted for the smaller dendrimer 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 and are very polar because the fragment trz-[FeII(η⁵-Cp)(η⁶-C₆H₂Me₃-)]PF₆ is very hydrophilic and soluble only in very polar solvents. Particularly, dendrimers and 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 and 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 and 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 PF₆⁻ anion of these salts shows a strong band in the range 836–842 cm⁻¹. The absorptions due to the 1H stretching of the triazole and Cp groups of the trz-[FeII(η⁵-Cp)(η⁶-C₆H₂Me₃-)]PF₆ unit are found in the range 3095–3127 cm⁻¹.
NMR spectroscopy confirms the structure of the trz-[Fe$^{II}(\eta^6$-Cp)(\eta$^6$-C$_6$H$_2$Me$_3$)]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$_3$OD or CD$_3$COCD$_3$) 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$^{II}(\eta^6$-Cp)(\eta$^6$-C$_6$H$_2$Me$_3$)]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, 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$^*$]$^{2+}$ and corresponds to the reduction of [Fe$^{II}$Cp(\eta$^6$-C$_6$H$_2$Me$_3$)]PF$_6$ to the 19-electron species [Fe$^{I}$Cp(\eta$^6$-C$_6$H$_2$Me$_3$)]. In all cases, this wave is single in DMF, which is explained by the
weakness of the electrostatic factor between the redox sites of the metallocendrimers, these redox centers being far from one another and separated by long tethers. 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 (O₂) atmosphere, the same phenomenon as that for the route to new cationic metallocendrimers and metal-complexes that parallels the cobalticenium family and opens electron-transfer steps.

The currently used click reaction, i.e., the Huisgen-type CuAAC, proves to be most useful to graft organometalllic complexes onto the periphery of dendrimers. 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 sensitivity to visible light and coordinating solvents such as acetonitrile, the polycationic metallocendrimers were fully characterized. The electron-withdrawing 1,2,3-triazolyl linkage 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, and/or the electron-hopping mechanism. The CV wave under N₂ of dendrimer 11 containing 27 [Fe³⁺(η⁵-C₅H₅)(η⁵-C₆H₂Me₃-)]PF₆ termini is shown in Figure 3.

**CONCLUDING REMARKS**

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⁺ 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(η⁵-C₅H₅)]PF₆ complexes that parallels the cobalticenium family and opens the route to new cationic metallocendrimers 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 31P NMR spectra were recorded in the pulsed FT mode at 100 MHz with a Bruker AVANCE 400 spectrometer. 31P 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 Me₄Si (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 GC-TOF 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 an 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, [nBu₄N][PF₆] 0.1M; working and counter electrodes, Pt; reference electrode, Ag; internal reference, FeCp*; 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/H₂O. At 0 °C, CuSO₄ 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 N₂. 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 (CD₃COCD₃, 400 MHz), δ (ppm): 8.41 (1H, CH of trz), 6.43 (2H, CH of mesitylene), 5.55 (2H of trz=CH₂), 5.17 (5H, CH of Cp of [Fe²⁺Cp(η⁵-C₅H₅)Me₃⁺])PF₆, 4.65 (2H, CH of Cp sub. of FeCp²⁺), 4.25 (2H, CH of Cp sub. and 5H, CH of Cp free of FeCp²⁺), 2.56 (3H, –CH₂CH₂), 2.35 (6H, trzCCCH₃), 1.23 (9H, trzCCCH₃). 31C NMR of 5 (CD₃COCD₃, 100 MHz), δ (ppm): 139.88 (Cq of trz), 125.86 (CH of trz), 102.80 (trz-Cq), 102.75 (trz-Cq).
Organometallics

94.44 (CH$_2$Q$_7$ of mesitylene), 88.48 (CH of mesitylene), 82.50 (CQ of Cp sub. of FeCp$_2$), 78.78 (CH of Cp of [FeIICp($^9$-C$_8$H$_{14}$Me$_3$)]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$_3$), 19.61 and 19.54 (−CH$_2$ of mesitylene). $^{19}$F NMR of 5 (CD$_2$COCD$_2$, 376 MHz), $\delta$ ppm: doublet centered at −73.3 ppm ($J_{F-P}$ = 710 Hz). $^{19}$P NMR of 5 (CD$_2$COCD$_2$, 162 MHz), $\delta$ ppm: −34.1 ppm (hept., PF$_6$ $^-$) ($J_{F-P}$ = 710 Hz). ESII MS of 5 (m/z): Calc. for C$_{23}$H$_{24}$F$_2$P$_2$F$_2$: 506.097 Da; found, 506.098 Da. Anal. Calc. for C$_{23}$H$_{24}$F$_2$P$_2$F$_2$: C, 49.80; H, 4.33. Found C, 50.10; H, 4.51.

**Complex 6.** A mixture of 1 equiv of S (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$_2$. 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, the product was obtained as a light-orange powder. Yield: 80% (19 mg).

**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 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 evaporated 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 sodium ascorbate. The reaction mixture was allowed to stir for 16 h at 60 °C under nitrogen atmosphere. 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 reaction 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. 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.

**Notes**

The authors declare no competing financial interest.

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Organometallics


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