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Branching the Electron-Reservoir Complex [Fe(η^5-C_5H_5)(η^6-C_6Me_6)][PF_6] onto Large Dendrimers: "Click", Amide, and Ionic Bonds

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Several strategies have been used to functionalize 1,3,5-trisubstituted arene-cored dendrimers with the organometallic electron-reservoir moiety [Fe(η^5-C_5H_5)(η^6-C_6Me_6)]$^+$, **1**, to provide dendritic multielectron reservoirs. They all start from the carboxylic acid [Fe(η^5-C_5H_4COOH)(η^6-C_6Me_6)][PF_6], **2**, or its acyl chloride derivative [Fe(η^5-C_5H_4COCl)-(η^6-C_6Me_6)][PF_6], **3**. For this purpose, a series of new polyamine dendrimers from G_0 to G_2 with 1→3 C connectivity of the branching to the core have been synthesized. Amide, "click" and ionic ammonium carboxylate linkage successfully provided G_0, G_1, and G_2 metallodendrimers with 9, 27, and 81 cationic terminal organoiron groups respectively. Further construction of large metallodendrimers up to G_7 with approximately 14 000 organoiron termini was only possible by combining amide, "click", and tether lengthening strategies to avoid steric bulk at the dendrimer periphery. Reduction of the 18-electron Fe^{II} metallodendrimers, exemplified by a G_4-DAB-64-Fe^{II} complex, was achieved exergonically using the parent electron-reservoir complex [Fe(η^5-C_5H_5)(η^6-C_6Me_6)], **1a**, at −30 °C in MeCN, which allowed further reduction of 64 equiv of C_{60} to $C_{60}^{\bullet-}$ using the 19-electron Fe^I metallodendrimer.

Introduction

Transition-metal sandwich complexes, the prototype of which is ferrocene, are well-known for their ability to contain flexible numbers of valence electrons on the metal center, unlike the other families of organometallic complexes.[1,2] This property is particularly marked for the late first-row transition-metal sandwich complexes because of the stereoelectronic properties of the delocalized π-cyclic ring ligands.[1,2] As a result, these complexes have rich redox properties that find applications as stoichiometric redox reagents,[3] redox catalysts,[4] electron-transfer-chain catalysts,[5] redox sensors,[6] electrochemical references,[7] and anticancer drugs.[8] The various redox potentials of these compounds span over the entire redox scale,[2,3] but some of them stand at very negative or very positive potentials. The reduced form of the former category serve as electron-reservoir systems (strong reductants), whereas the oxidized form of the later category serve as reservoirs of electron holes (strong oxidants).[2] The mixed-sandwich complexes [Fe(η^5-C_5H_5)(η^6-C_6Me_6)]$^{n+}$, (**1** for n = 1, **1a** for n = 0), have the property to serve as either electron reservoirs for the redox couple involving n = 1/0[9] or reservoirs of electron holes for n = 2/1.[10] Indeed, the family of 18-electron complexes [Fe(η^5-C_5H_5)(η^6-arene)]$^+$ is very large because of the reactivity of the coordinated arene that is activated by the cationic 12-electron group CpFe$^+$.[11] A key

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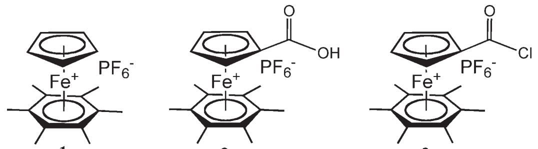
property of this series of complexes was found in the electron-reservoir properties of the 19-electron neutral Fe^{I} complexes $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})]$ that are only useful if the arene ligand is peralkylated, in particular with hexamethylbenzene.[12] A carboxylic acid derivative of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ could be obtained upon carrying out ligand exchange of the unsubstituted cyclopentadienyl ring of ferrocenecarboxylic acid by hexamethylbenzene in the presence of CO_2 and aluminum chloride. The resulting complex $[Fe(\eta^5\text{-}C_5H_4{-}COOH)(\eta^6\text{-}C_6Me_6)][PF_6]$, **2**, allowed further functionalization of the stable electron-reservoir complexes through reaction of its acyl chloride derivative $[Fe(\eta^5\text{-}C_5H_4COCl)(\eta^6\text{-}C_6Me_6)][PF_6]$, **3** with amines, alcohols, and thiols.[13]



1 **2** **3**

Metallodendrimers have a very rich chemistry that has been largely reviewed.[14,15] Our group have been interested in studying the redox properties of different types of metallodendrimers, including giant ferrocenyl[16] and cobaltocenyl[17] dendrimers. However, our efforts to attach the $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)][PF_6]$ complex to the periphery of dendrimers have been marred by insolubility problems, as shown in a previous communication.[18] Branching of iron-sandwich complexes in which the arene ligand was not fully permethylated was also reported to be easier, but without hope to form stable Fe^{I} complexes.[19] The inclusion of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^+$ into dendrimers was a high synthetic challenge because of the combination of the positive charge and large bulk and rigidity of the arene in the mixed-sandwich complex.

We now report several synthetic strategies used to attach $[Fe(\eta^5\text{-}C_5H_4R)(\eta^6\text{-}C_6Me_6)]^+$ moieties onto periphery of the dendrimers. New amino-terminated dendrimers were synthesized and used to provide amide links and ionic bonding, upon reactions with the organometallic acyl chloride **3** and carboxylic acid **2** respectively with up to 81 termini. Tether lengthening of polyallyl dendrimers to form long-arm azido-terminated dendrimers allowed the synthesis of giant metallodendrimers by "click" chemistry with propargylated organoiron groups. Only the later bond-lengthening route allows avoiding the bulk problems for these metallodendrimer syntheses above the second generation (G_2), up to G_7 with a theoretical number of 19683 termini.

Results and Discussion

1. Synthesis of the Dendrimer Series. Our synthetic strategy to build our series of dendrimers follows the 1→3 C connectivity.[20] The dendritic construction starts with the known nona-allylation of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-mesitylene})][PF_6]$, followed by visible-light photolysis to remove the metal moiety,[21a,b] quantitatively yielding the nona-allyl dendritic core G_0-9-allyl, **4**.[21c−e] Hydrosilylation of the terminal olefinic bonds of G_0-9-allyl, using $HSi(CH_3)_2CH_2Cl$ and the Karstedt catalyst, regioselectively gives the nona-chloromethyl(dimethyl)silyl derivative, **5**. Williamson reaction between **5** and the phenoltriallyl

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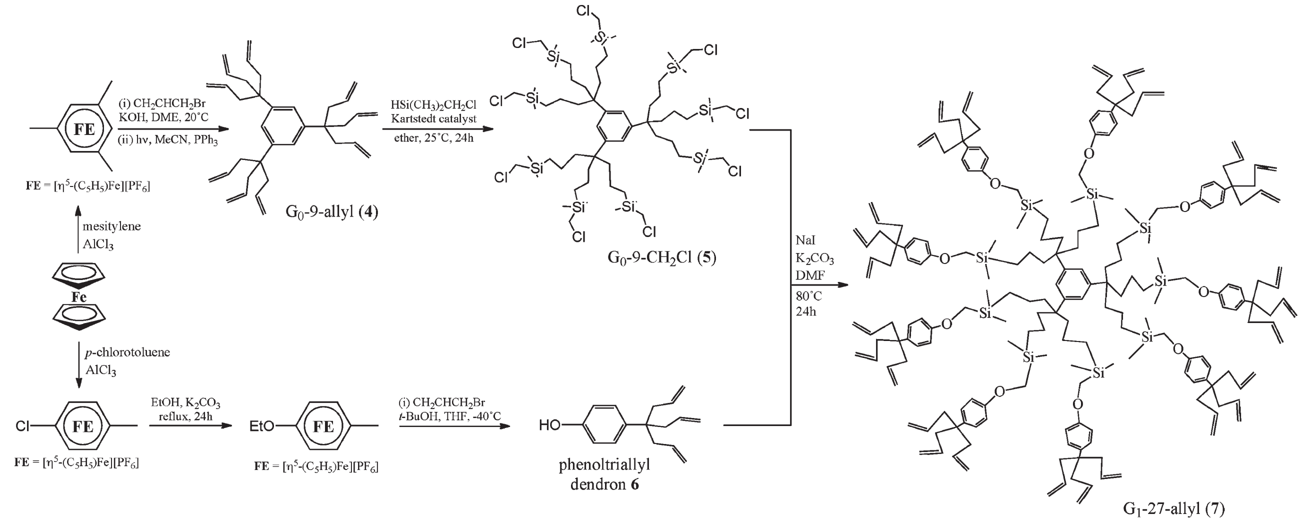
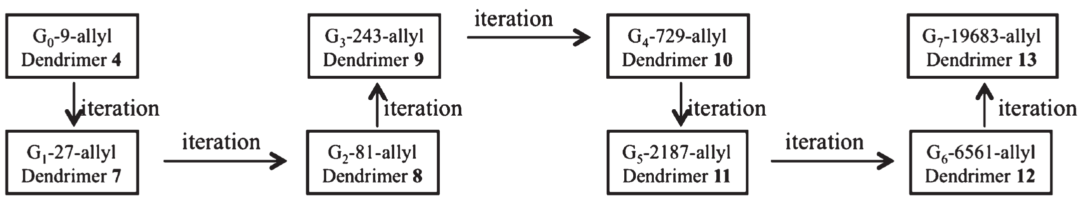
Scheme 1. Synthesis of the Nona-Allyl Core **4**, Phenoltriallyl Dendron **6**, and G_1-27-allyl **7**



Scheme 2. Construction of the Series of Allyl Dendrimers[a]



[a] The syntheses of the G_n-3^{n+2}-allyl (n = 0-7) dendrimers follows the iteration reactions shown in Scheme 1: hydrosilylation reaction and Williamson reaction using the phenoltriallyl dendron.[23].

dendron **6**,[22] afforded the first-generation (G_1) dendrimer containing 27 allyl termini, **7** (Scheme 1).[23]

Repetition of the sequence of reactions (iteration) involving hydrosilylation of the allyl dendrimers followed by coupling with the phenoltriallyl dendron **6**, until G_9, afforded the series of giant pentane-soluble allyl-terminated dendrimers (Scheme 2).[23]

2. Functionalization of the Organic Dendrimers with the Organoiron Cation [Fe(η^5-C_5H_5)(η^6-C_6Me_6)]$^+$. 2.1. New Dendritic Amines and Branching the Organoiron Cation with Amide and Ionic Linkage, up to 81 Termini. 2.1.1. Synthesis of New Polyamine Dendrimers. Amine-terminated dendrimers were synthesized from the chloromethyl-terminated dendrimers in two steps: (i) nucleophilic substitution of the terminal chloride by azide using NaN_3, affording the polyazide dendrimers;[24] (ii) reduction of the azide termini using either PPh_3/H_2O or $LiAlH_4$. Both reductants give quantitative yields, but the use of $LiAlH_4$ is preferred to avoid the difficult separation of the amine dendrimers from PPh_3 and $O=PPh_3$ (this later species resulting from reduction of the azide groups with PPh_3/H_2O). This synthesis was carried out for G_n-3^{n+2}-NH_2 (n = 0−2), providing polyamine dendrimers that contain respectively 9 (G_0-9-NH_2, **14**), 27 (G_1-27-NH_2, **15**), and 81 (G_2-81-NH_2, **16**) terminal primary amine groups (Chart 1). The nona-amine **14** is soluble in water, unlike **15** and **16**, and the three polyamine dendrimers are soluble in ether, dichloromethane, and chloroform.

Polyamine dendrimers have important applications as largely known with poly(amidoamine) (PAMAM), poly(propylene imine) (PPI), and melanine dendrimers.[14a−d,25]

2.1.2. Attachment of the Complex [Fe(η^5-$C_5H_4CO_2H$)(η^6-C_6Me_6)][PF_6] to Amine Dendrimers through Covalent Amide Linkages. It was found that the reaction between the acid derivative **2** and amine groups gave optimal yields when the acyl chloride derivative **3** ([Fe(η^5-C_5H_4-COCl)(η^6-C_6Me_6)][PF_6]) was freshly prepared by refluxing **2** overnight in thionyl chloride, and then added to a dichloromethane solution of the amine compound in presence of triethylamine.[13,18] Reactions of propylamine (**17**) and the polyamine dendrimers **14** and **15** with the acyl chloride **3** yielded the monomeric compound [Fe(η^5-C_5H_4CONHPr)(η^6-C_6Me_6)][PF_6], **18** and the dendritic complexes G_0-9-[Fe(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)][PF_6], **19**, and G_1-27-[Fe(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)][PF_6], **20** as orange powders (eq 1 and Chart 2). The dendritic complexes are soluble in dichloromethane, acetonitrile, and dimethylformamide, but not in ether nor water.

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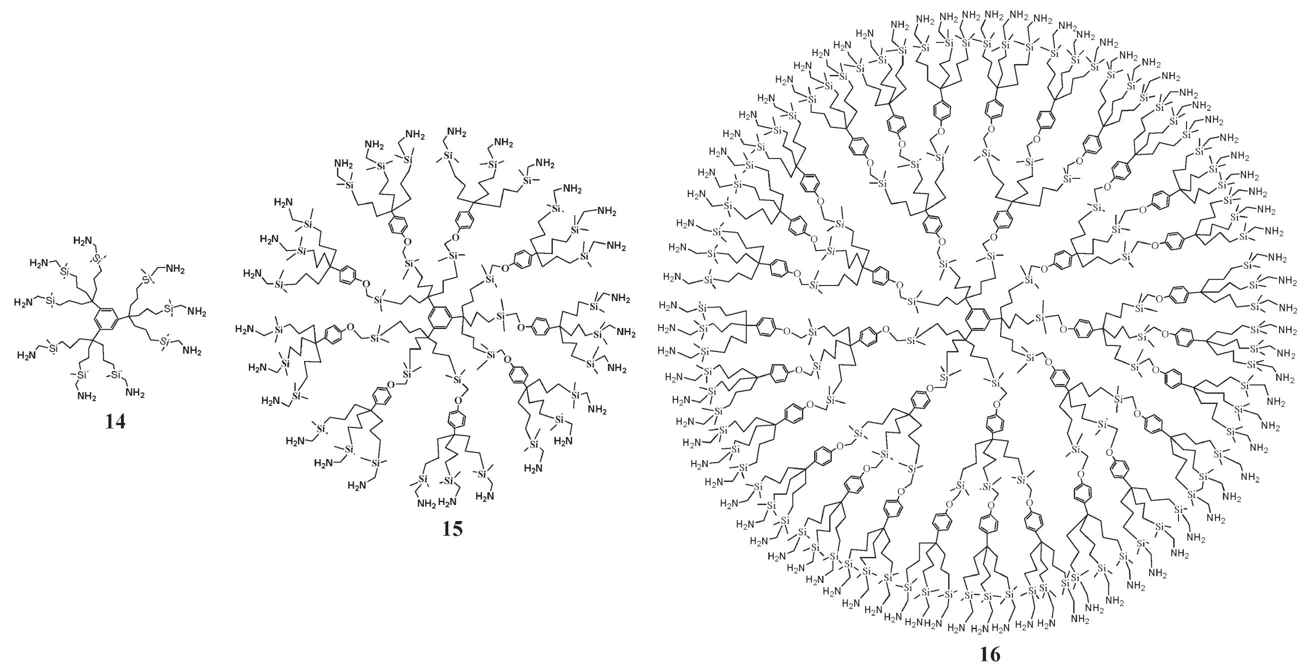
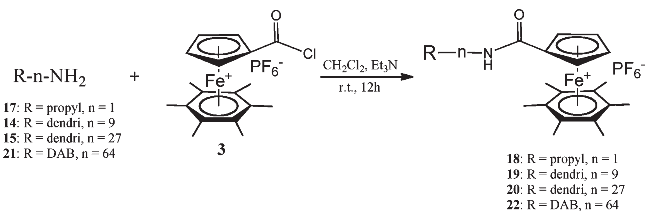
Chart 1. Three Generations G_0-G_2 of Amine-Terminated Dendrimers



For comparison, we also carried out the reaction between the commercially available diaminobutane (DAB) dendrimer G_4-DAB-64-NH_2, **21**, and **3** in $MeCN/CH_2Cl_2$ (2:1) in the presence of triethylamine, yielding the dendritic complex G_4-DAB-64-[(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)][PF_6], **22**, as an orange powder with similar solubility properties.



2.1.3. Ionic Binding between the Polyammonium Dendrimers and Two Organoiron Carboxylates [Fe(η^5-C_5H_4-CO_2H)(η^6-C_6Me_6)][PF_6] and [Fe(η^5-$C_5H_4CO_2H$)(η^5-C_5H_5)]. The formation of dendritic ammonium carboxylates from dendritic amines and carboxylic acid is precedented.[14a−d,26] This property was used to bind complex **2** to the amine dendrimers through ionic bonds (eq 2). Propylamine **17** and the polyamine dendrimers **14**, **15**, and **16** were mixed with [Fe(η^5-$C_5H_4CO_2H$)(η^6-C_6Me_6)][PF_6], **2**, in MeCN at room temperature under inert atmosphere, affording respectively the monomeric salt **23** and the dendritic polyammonium carboxylates **24**, **25,** and **26** (Chart 3) as orange powders that were characterized by ^{1}H and ^{13}C NMR, IR, and elemental analysis.

$$R'NH_2 + R''CO_2H \rightarrow R''CO_2{}^- \text{-----} {}^+NH_3R' \qquad (2)$$

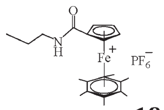
For comparison, the ionic binding of the neutral iron complex ferrocenecarboxylic acid, **27**, to propylamine and polyamine dendrimers has also been studied. Ferrocenecarboxylic acid **27** was mixed with propylamine stoichiometrically in tetrahydrofuran (THF), which allowed precipitation of an orange solid, **28**. The same reaction was carried out with the three dendritic amines G_0-9-NH_2, G_1-27-NH_2, and G_2-81-NH_2 also resulting in the formation of the polyammonium carboxylates **29**, **30**, and **31** as orange powders (Chart 3). These compounds were soluble only in acetone and slightly so in methanol. They were characterized by IR (in KBr) and ^{1}H NMR spectroscopy (rapidly recorded spectra in CD_3COCD_3).

Table 1 shows the comparative NMR and IR data for the carboxylic acid **2**, the carboxylate sodium salt [Fe(η^5-$C_5H_4CO_2{}^-Na^+$)(η^6-C_6Me_6)][PF_6], **2a**, the carboxylate propylammonium salt [Fe(η^5-$C_5H_4CO_2{}^-PrNH_3{}^+$)(η^6-C_6Me_6)][PF_6], **23**, and the dendritic ammonium salts [Fe(η^5-$C_5H_4CO_2{}^-$dendr$NH_3{}^+$)(η^6-C_6Me_6)][PF_6], **24**−**26**.

The IR carbonyl bands of the acid complex **2** at 1702 and 1618 cm^{-1} are shifted to 1630 and 1580 cm^{-1} for the sodium carboxylate salt **2a**; likewise they are found at 1634 and 1591 cm^{-1} for the propylammonium as well as for the dendritic ammonium salts, suggesting the expected protonation of the primary amino group by the carboxylic acid. In ^{1}H NMR, the proton signals of the substituted cyclopentadienyl ligand of acid **2** are found at 4.97 ppm for the β proton and at 4.79 ppm for the γ proton, and these signals are shifted to 4.73 ppm and 4.45 ppm, respectively, for the sodium carboxylate salt. The corresponding proton signals on the propyl- and dendritic ammonium salts are found at 4.73−4.77 ppm and 4.55−4.58 ppm, that is, intermediate between those of the acid **2** and those of the sodium carboxylate **2a**, probably because of hydrogen bonding between the primary ammonium and the carboxylate group. The ^{1}H signal of the methylene group that is bound to the amino group is found at 2.60 ppm for propylamine and 2.14 ppm for the dendrimers, and it is shifted downfield to 2.98 ppm for the propylammonium and to 2.40 ppm for the polyammonium

(26) (a) Ornelas, C.; Boisselier, E.; Martinez, V.; Pianet, I.; Aranzaes, J. R.; Astruc, D. *Chem. Commun.* **2007**, 5093–5095. (b) Boisselier, E.; Ornelas, C.; Pianet, I.; Aranzaes, J. R.; Astruc, D. *Chem.—Eur. J.* **2008**, *14*, 5577–5587.

Chart 2. Metallodendrimers Synthesized through Amide Linkages According to Equation 1



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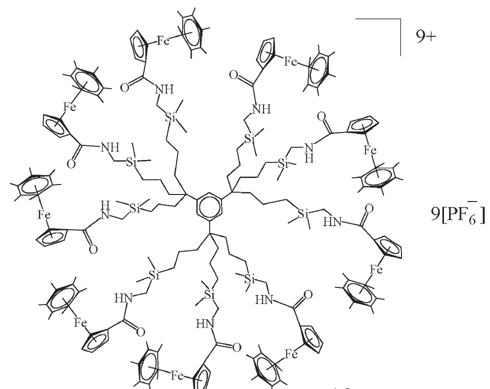

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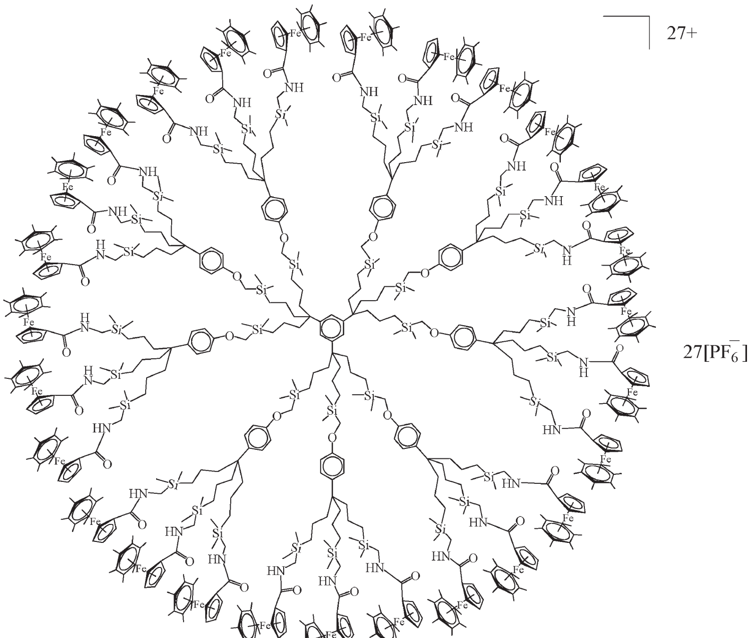

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dendrimers. All these IR and NMR data are in agreement with the dendritic ammonium carboxylate formulation.

Table 2 shows the ^{1}H NMR and IR data for the ferrocenecarboxylic acid **27**, the carboxylate propylammonium salt [Fe(η^5-$C_5H_4CO_2^-PrNH_3^+$)(η^5-C_5H_5)], **28**, and the dendritic ammonium salts [Fe(η^5-$C_5H_4CO_2^-$-dendrNH_3^+)(η^5-C_5H_5)], **29**−**31**, recorded in $(CD_3)_2CO$. Table 3 shows the ^{1}H, ^{13}C NMR and IR data for the sodium ferrocenecarboxylate salt **27a** and the carboxylate propylammonium salt [Fe(η^5-$C_5H_4CO_2^-PrNH_3^+$)(η^5-C_5H_5)], **28**, recorded in D_2O.

The IR carbonyl band of ferrocenecarboxylic acid, **27**, at 1657 cm^{-1} is shifted to 1533 cm^{-1} in the carboxylate sodium salt, **27a**, 1518 cm^{-1} for the propylammonium salt, **28**, and 1545 to 1548 cm^{-1} for the dendritic polyammonium ferrocenenecarboxylate salts **29**−**31**. Similarly to the ionic binding of iron complex **2**, the ionic binding of ferrocenecarboxylic acid with the polyamine dendrimers shows an upfield shift on the ^{1}H NMR signals of the cyclopentadienyl protons adjacent to the acid group from 4.80 ppm to 4.73 ppm (Table 2). ^{13}C NMR spectra of the ionic dendritic ferrocenyl derivatives could not be carried out satisfactorily because acetone slowly reacts with them during the time necessary for recording the ^{13}C NMR spectra, and the solubility in CD_3OD is not sufficient. ^{13}C NMR spectra could be recorded in D_2O for the sodium and propylammonium carboxylate salts **27a** respectively **28**. The data gathered in Tables 2 and 3 strongly suggests the formation of the ferrocenylcarboxylate salts of propylammonium **28** and dendritic polyammonium **29**−**31**.

2.2. Attachment of the Complex [Fe(η^5-C_5H_4R)(η^6-C_6Me_6)][PF_6] to Giant Dendrimers up to 14 000 Termini: Tether Lengthening and "Click" Reaction. Several attempts to attach complex **1** to giant dendrimers through amide coupling reaction have failed, mainly because of the quick insolubilization of the high generation amine-terminated dendrimers, with or without long tethers.

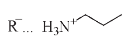
The concept of "click chemistry" was introduced by Sharpless and co-workers in 2001[27] and among the "click" reactions, the Cu(I)-catalyzed alkyne azide 1,3-dipolar cycloaddition (CuAAC) is the most popular.[28] CuAAC was successfully applied in different areas of materials chemistry,[29] including dendrimers.[30] In dendrimer chemistry, CuAAC was used for the convergent[30a] and divergent[6k] syntheses as well as in their functionalization.[24,30b−30d] The continuous success of this reaction inspired us in the development of a new synthetic strategy to attach the iron complex **1** to giant dendrimers that include: (i) lengthening of the allyl dendrimers tethers using a silane with a long chain and a bromo termini, followed by substitution of the bromide termini by azide groups; (ii) functionalization of complex **1** with alkyne termini; and (iii) CuAAC reaction between the giant-long azide dendrimers with the alkyne iron complexes.

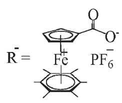
2.2.1. Synthesis of New Polyazido Dendrimers with Lengthened Tethers. A silane compound with a long chain and a bromo termini, 11-bromoundecyl(dimethyl)silane, **32**, was synthesized by hydrosilylation of bromo-1-undecene with (dimethyl)chlorosilane followed by $LiAlH_4$ reduction (scheme 3).

The tethers of the polyallyl dendrimers **4**, **7**, **10**, and **13** (G_0, G_1, G_4, and G_7) with 9, 27, 729, and 19683 termini

(27) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.
(28) Meldal, M.; Tornoe, C. W. *Chem. Rev.* **2008**, *108*, 2952–3015.
(29) (a) Meldal, M. *Macromol. Rapid Commun.* **2008**, *29*, 1016–1051. (b) Boisselier, E.; Diallo, A. K.; Salmon, L.; Ruiz, J.; Astruc, D. *Chem. Commun.* **2008**, 4819–4821. (c) Durot, S.; Mobian, P.; Collin, J. P.; Sauvage, J. P. *Tetrahedron* **2008**, *64*, 8496–8503. (d) Megiatto, J. D.; Schuster, D. I. *J. Am. Chem. Soc.* **2008**, *130*, 12872–12873.
(30) (a) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 3928–3932. (b) Joralemon, M. J.; O'Reilly, R. K.; Matson, J. B.; Nugent, A. K.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **2005**, *38*, 5436–5443. (c) Srinivasachari, S.; Fichter, K. M.; Reineke, T. M. *J. Am. Chem. Soc.* **2008**, *130*, 4618–4627. (d) For a review on "click" dendrimers: Franc, G.; Kakkar, A. *Chem. Commun.* **2008**, 5267–5276.

Chart 3. Polyammonium Carboxylates Generated by Mixing the Carboxylic Acid Complexes **2** and **27** with the Polyamine Dendrimers

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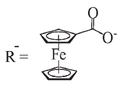
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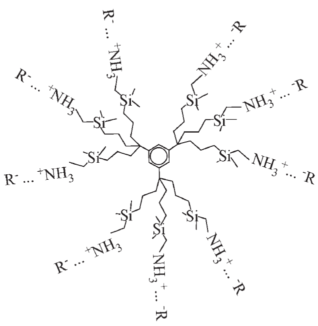

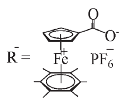
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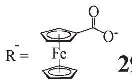
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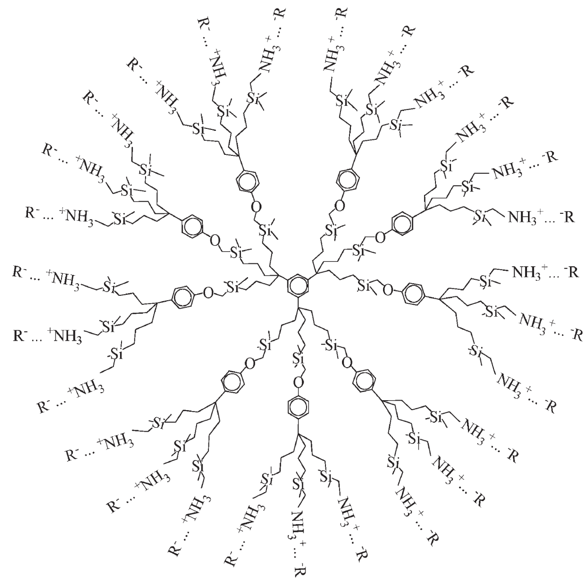

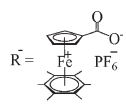
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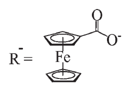
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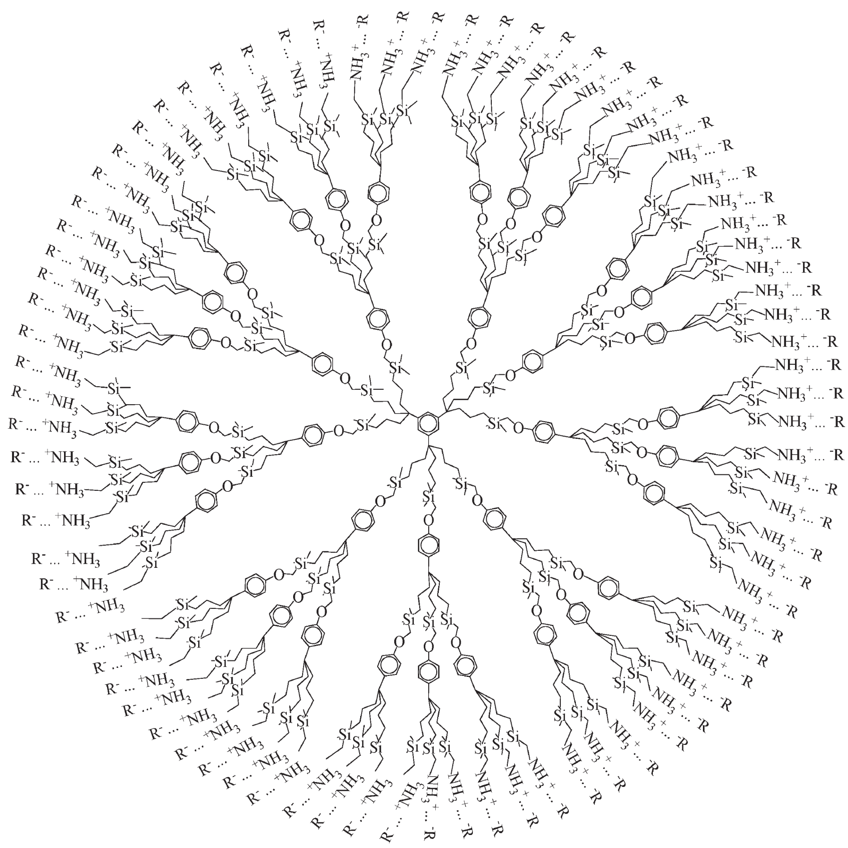

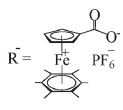
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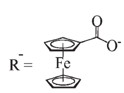
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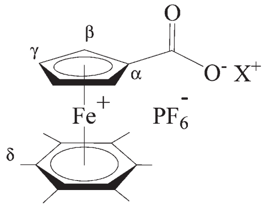
respectively, were lengthened by hydrosilylation reaction with the silane **32**. The bromo group of the bromoalkyl-terminated dendrimers was subsequently substituted by an azido group upon nucleophilic substitution using

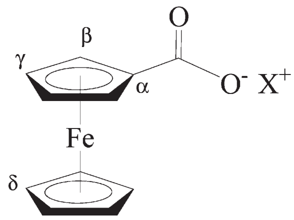
Table 1. [1]H, [13]C NMR, and IR Data of the Complexes Obtained by Mixing [Fe(η^5-$C_5H_4CO_2H$)(η^6-C_6Me_6)][PF_6], **2**, with Propylamine **17** and the Amino-Terminated Dendrimers **14**−**16**, in CDCN



2a: X^+= Na^+
23: X^+= Pr-NH_3^+
24: X^+= G_0-9-NH_3^+
25: X^+= G_1-27-NH_3^+
26: X^+= G_2-81-NH_3^+

compound	$^1H_\beta/^{13}C_\beta$ δ(ppm)	$^1H_\gamma/^{13}C_\gamma$ δ(ppm)	$^1H/^{13}C(CH_2NH_3^+)$ δ(ppm)	IR- CO(cm^{-1}) KBr
[Fe(η^5-$C_5H_4CO_2H$)(η^6-C_6Me_6)][PF_6], **2**	4.97/80.7	4.79/78.2		1702; 1618
[Fe(η^5-$C_5H_4CO_2^-Na^+$)(η^6-C_6Me_6)][PF_6], **2a**	4.73/79.1	4.45/78.4		1630; 1580
Pr-NH_2, **17**			2.60/43.9	
[Fe(η^5-$C_5H_4CO_2^-PrNH_3^+$)(η^6-C_6Me_6)][PF_6], **23**	4.73/79.3	4.55/78.3	2.98/	1634; 1591
G_0-9-NH_2, **14**			2.14/29.9	
G_0-9-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)(η^6-C_6Me_6)][PF_6], **24**	4.73/79.5	4.58/78.2	2.40/27.1	1634; 1591
G_1-27-NH_2, **15**			2.14/30.6	
G_1-27-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)(η^6-C_6Me_6)][PF_6], **25**	4.76/79.6	4.58/78.2	2.40/27.0	1634; 1591
G_2-81-NH_2, **16**			2.14/30.0	
G_2-81-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)(η^6-C_6Me_6)][PF_6], **26**	4.77/79.8	4.58/78.2	2.40/27.0	1634; 1591

Table 2. [1]H NMR and IR Data of the Complexes Obtained by Mixing [Fe(η^5-$C_5H_4CO_2H$)(η^5-C_5H_5)], **27**, with Propylamine **17** and Amino-Terminated Dendrimers **14**−**16**, in $(CD_3)_2CO$



27a: X^+= Na^+
28: X^+= Pr-NH_3^+
29: X^+= G_0-9-NH_3^+
30: X^+= G_1-27-NH_3^+
31: X^+= G_2-81-NH_3^+

compound	$^1H_\beta$ δ(ppm)	$^1H_\gamma$ δ(ppm)	^1H ($CH_2NH_3^+$) δ(ppm)	IR- CO(cm^{-1}) KBr
[Fe(η^5-$C_5H_4CO_2H$)Cp], **27**	4.80	4.50		1657
Pr-NH_2, **17**			2.64	
[Fe(η^5-$C_5H_4CO_2^-PrNH_3^+$)Cp], **28**	4.72	4.40	3.13	1518
G_0-9-NH_2, **14**			2.14	
G_0-9-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)Cp], **29**	4.73	4.36	2.04	1545
G_1-27-NH_2, **15**			2.14	
G_1-27-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)Cp], **30**	4.73	4.34	2.04	1548
G_2-81-NH_2, **16**			2.14	
G_2-81-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)Cp], **31**	4.73	4.39	3.04	1548

Table 3. [1]H, [13]C NMR and IR Data of the Sodium Ferrocenecarboxylate Salt **27a** and the Carboxylate Propylammonium Salt [Fe(η^5-$C_5H_4CO_2^-PrNH_3^+$)(η^5-C_5H_5)], **28**, in D_2O

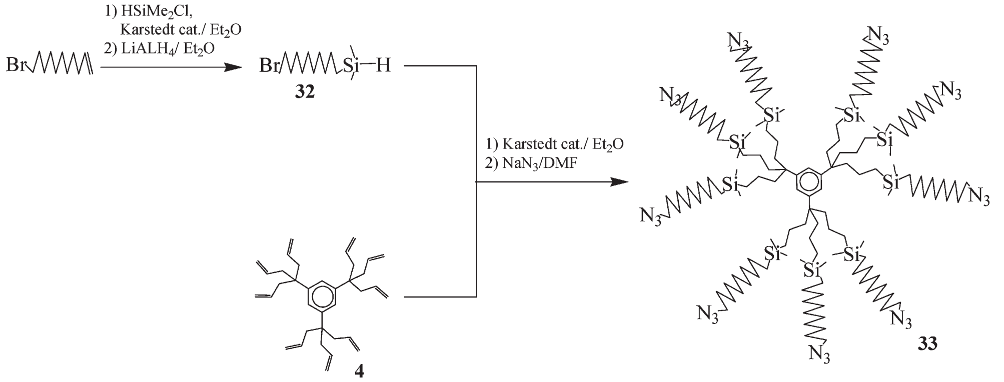
compound	$^1H_\beta/^{13}C_\beta$ δ(ppm)	$^1H_\gamma/^{13}C_\gamma$ δ(ppm)	$^1H/^{13}C(CH_2NH_3^+)$ δ(ppm)	IR- CO(cm^{-1}) KBr
[Fe(η^5-$C_5H_4CO_2^-Na^+$)(η^5-C_5H_5)], **27a**	4.59/76.3	4.36/70.7		1533
Pr-NH_2, **17**			2.64/42.7	
[Fe(η^5-$C_5H_4CO_2^-PrNH_3^+$)(η^5-C_5H_5)], **28**	4.61/70.73	4.37/70.01	2.90/40.9	1518

sodium azide, affording the new long-arm polyazide dendrimers **33** (G_0-long-9-N_3), **34** (G_1-27-long-N_3), **35** (G_4-729-long-N_3), and **36** ($(G_7$-19683-long-$N_3)_{19683}$) (Scheme 3).

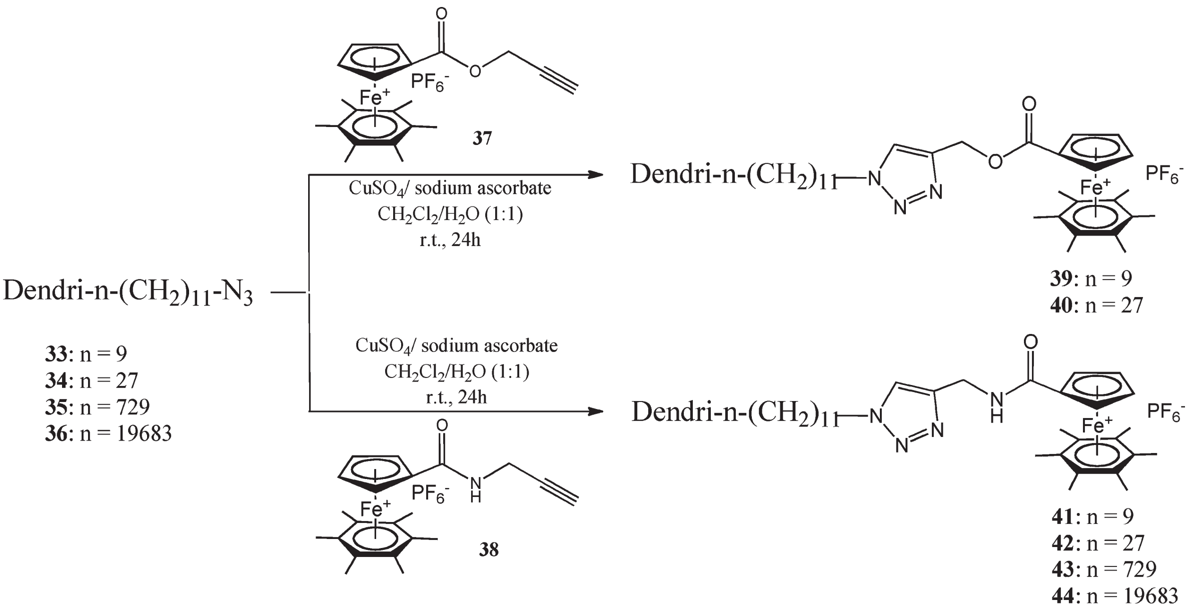
2.2.2. Synthesis of the Alkyne Derivatives of Complex 1. Two alkyne derivatives of complex **1** were obtained by coupling reaction between freshly prepared [Fe(η^5-C_5H_4-COCl)(η^6-C_6Me_6)][PF_6], **3**, and propagyl amine and propargyl alcohol (following the same procedure shown on eq 1). The new propargyl ester and propargyl amide complexes [Fe(η^5-$C_5H_4CO_2CH_2C{\equiv}CH$)($\eta^6$-$C_6Me_6$)][$PF_6$], **37**, and [Fe($\eta^5$-$C_5H_4CONHCH_2C{\equiv}CH$)($\eta^6$-$C_6Me_6$)][$PF_6$], **38**, were obtained in high yields and fully characterized (Scheme 4).

2.2.3. CuAAC Reactions between the Giant Azide Dendrimers and Alkyne Derivatives of the Iron Complexes. The CuAAC reaction between the iron complexes **33** and **34** with the new long-arm polyazide-terminated dendrimers was carried out in CH_2Cl_2/H_2O (1:1), using $CuSO_4$/sodium ascorbate as the Cu^I source. The completion of all the "click" reactions was verified by IR spectroscopy by the disappearance of the azide band at 2097 cm^{-1}, and by [1]H NMR showing the appearance of the new triazole

Scheme 3. Synthesis of the Long-Arm Polyazide Dendrimers, Example of G_0



Scheme 4. CuAAC Reaction between the Long-Arm Azido Dendrimers and the Propargyl Iron Complexes Yielding the "Click" Metallodendrimers



protons at 7.99 ppm and the disappearance of the CH_2N_3 signal at 3.25 ppm.

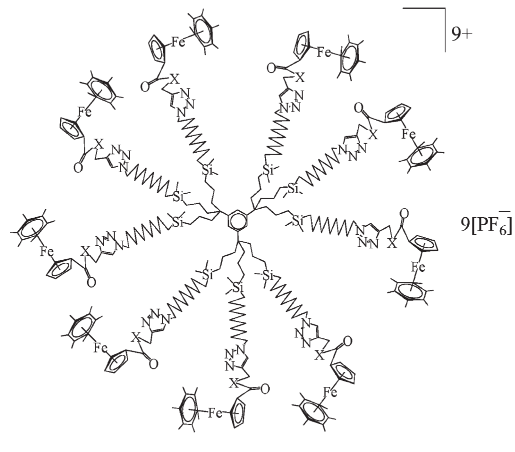
When using the propargyl ester iron complex **37**, the "click" reaction easily afforded the metallodendrimers **39** and **40** bearing 9 and 27 $[Fe(\eta^5\text{-}C_5H_4CO_2R)(\eta^6\text{-}C_6Me_6)][PF_6]$ complexes, respectively (Scheme 4 and Chart 4). Attempts to synthesize the G_2 analogue (81 termini), led to characterization by IR showing the absence of the azido band and by ^1H NMR, including the observation of the triazole protons, indicating completion of the "click" reaction. However, the compound became completely insoluble in all solvents after recording the ^1H NMR spectrum in CD_3CN, thus, record of the ^{13}C NMR spectrum and further characterization were not possible.

For the "click" reactions carried out with the propargyl amide iron complex **38**, four generations of metallodendrimers bearing theoretical numbers of 9, 27, 729, and 19 683 $[Fe(\eta^5\text{-}C_5H_4CO_2R)(\eta^6\text{-}C_6Me_6)][PF_6]$ species respectively (**41**−**44**) were obtained as orange powders that were completely soluble in acetone (Scheme 4 and Chart 4). The high solubility of these "click" metallodendrimers allowed their characterization by ^1H and ^{13}C NMR, UV−vis spectroscopy, cyclic voltammetry (CV), and dynamic light scattering (for the higher generations). These compounds only became completely insoluble orange solids after several days of storage at air conditions and room temperature.

3. Characterization of the Metallodendrimers. All the metallodendrimers reported here were characterized by ^1H and ^{13}C NMR, elemental analysis, UV−vis spectroscopy, and CV. Dynamic light scattering was used to measure the size of the giant metallodendrimers **43** and **44**.

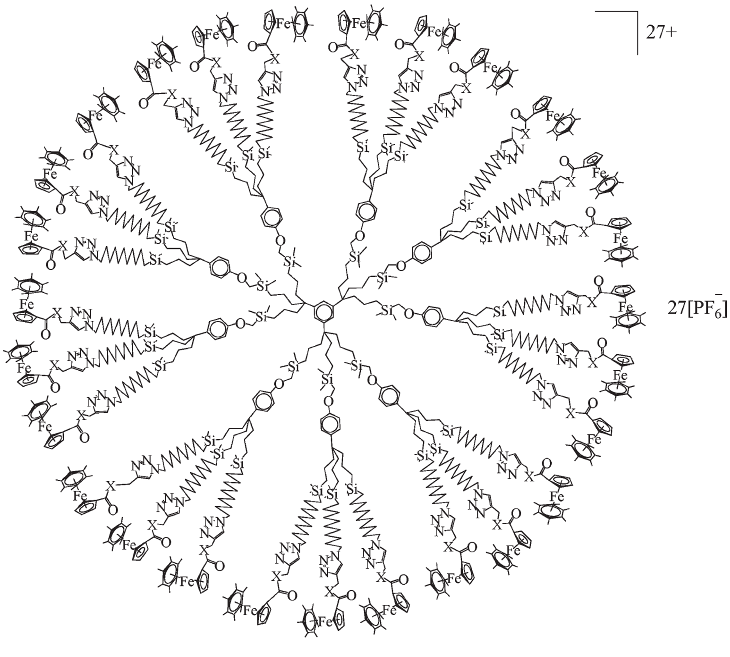
3.1. UV−vis of the Metallodendrimers. As expected, the metallodendrimers bearing the complex $[Fe(\eta^5\text{-}C_5H_4COR)(\eta^6\text{-}C_6Me_6)][PF_6]$ present an absorption band at 411−416 nm in the UV−vis spectra. This band is located at 416 nm for the amide derivatives, 413 nm for the ester derivatives, and 411 nm for the carboxylate complexes (Table 4). It was possible to estimate the number of terminal organoiron groups by UV−vis spectroscopy using the Lambert−Beer law, from the $\varepsilon/\varepsilon_0$ ratio between the molar extinction coefficient ε of the dendritic complex and that of the monomer, ε_0 (Table 4). The estimated number of terminal groups are in agreement with the expected structures up to G_4, but much lower than the theoretical value for G_7. This result was expected because of the large amounts of defects formed in the divergent construction. Similar agreements and discrepancies were

Chart 4. Metallodendrimers G_0 and G_1 Synthesized by CuAAC Reactions



39: X=O

41: X=NH



40: X=O

42: X=NH

observed for the ferrocenyl dendrimers, indicating that the divergent construction is responsible for the defects rather than the final metal-loading step. The discrepancies become very large only with G_7 (14000 ± 1000 terminal organoiron groups for a theoretical number of 19683). In addition, G_7 also presents the maximum ability to encapsulate inorganic salt impurities.[16]

3.2. Dynamic Light Scattering of the Giant Metallodendrimers. Dynamic Light Scattering (DLS) is a very useful technique to characterize the giant metallodendrimers because it allows to determine the size (hydrodynamic diameter) of the dendrimers in solution, and consequently calculate their diffusion coefficient (D) using the Stokes−Einstein equation: $D = kT/6\pi\eta R_h$, where R_h is the hydrodynamic radius, η is the solvent viscosity, k is the Boltzmann's constant, and T is the temperature. It is known that high-generation dendrimers present globular shapes and, along the search of their physical properties, they are often assimilated to perfect spheres.[17a−d] We also used this approximation to calculate the volume and the density of the metallodendrimers **43** and **44** (Table 5).

3.3. Cyclic Voltammetry. All the covalent and ionic metallodendrimers containing the organoiron group [Fe(η^5-C_5H_4COR)(η^6-C_6Me_6)][PF_6] were studied by CV using DMF as the solvent, [n-Bu_4][PF_6] as the supporting electrolyte, and decamethylferrocene as the internal reference. A single reversible CV wave was observed, corresponding to the cathodic reduction $Fe^{II} \rightarrow Fe^{I}$ (Figure 1 and Table 6). This CV wave is known from several reports for the family of monometallic complexes [Fe(η^5-C_5H_5)(η^6-arene)][PF_6].[3,4a,12,31] Table 6 gathers the data for all the compounds reported here. The CV wave is seemingly chemically and electrochemically reversible, but its observation was more or less marred by adsorption, and attempts to measure the number of electrons involved in the electron-transfer process did not work above G_0, unlike with the ferrocenyl dendrimers (UV−vis spectroscopy was more appropriate for this purpose for the present family of compounds).

4. Reduction to Dendritic 19-Electron Fe^I Complexes and Multielectron-Reservoir Properties. Although several functional complexes of this family could be reduced to stable Fe^I, 19-electron complexes, dendritic branching is less favorable for the stability of these compounds. For instance, reduction of G_0-9-[Fe(η^5-$C_5H_4CO_2$dendr)(η^6-C_6Me_6)][PF_6], **41**, by the 19-electron complex **1** led to decomplexation of the organoiron sandwich fragment in the dendrimer, as indicated by the finding of the decoordinated arene C_6Me_6 in ^{1}H NMR.

Attempts to reduce the dendrimer **22** using Na/Hg or $LiAlH_4$ in THF or dimethyl ether (DME) failed because of the insolubility of both this dendritic 18-electron complex and the reductant in these solvents. The only reductant that proved to be efficient to reduce **22** was the 19-electron complex **1a**. This electron-reservoir complex **1** has a redox potential of the $Fe^{II/I}$ couple that is 0.15 V more negative than that of the dendritic complex **22** because of the presence of the electron-withdrawing amido link on the cyclopentadienyl group of **22**. Thus, stoichiometric reduction of the dendritic 18-electron complex **22** in MeCN using 64 equiv of complex **1a** gave the dendritic 19-electron complex **22a** (Scheme 5). The complex **22a** shows the typical deep-blue-green color of such 19-electron complexes, and it was also characterized by electron paramagnetic resonance (EPR) at 10 K (Figure 2), showing the classic rhombic distorted signal. The complex **22a** decomposed around 0 °C.[12a,18,32]

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Table 4. UV−vis Data for the Dendritic Complexes and Estimated Number of Metalated Branches Using the Lambert−Beer Law

complex	λ (nm)	theoretical number of branches	ε	calculated number of branches ($\varepsilon/\varepsilon_0$)
Covalent Bonds				
$[Fe(\eta^5\text{-}C_5H_4CONHCH_2CCH)(\eta^6\text{-}C_6Me_6)][PF_6]$, **38**	416	1	ε_0 = 151	
G_0-9-$[Fe(\eta^5\text{-}C_5H_4CONH\text{-})(\eta^6\text{-}C_6Me_6)][PF_6]$, **19**	416	9	12300	9 ± 1
G_1-27-$[Fe(\eta^5\text{-}C_5H_4CONH\text{-})(\eta^6\text{-}C_6Me_6)][PF_6]$, **20**	416	27	4080	27 ± 1
$[Fe(\eta^5\text{-}C_5H_4CONHCH_2CCH)(\eta^6\text{-}C_6Me_6)][PF_6]$, **38**	416	1	ε_0 = 151	
G_0-9-$[Fe(\eta^5\text{-}C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-$)(\eta^6\text{-}C_6Me_6)][PF_6]$, **41**	416	9	1340	9 ± 1
G_1-27-$[Fe(\eta^5\text{-}C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-$)(\eta^6\text{-}C_6Me_6)][PF_6]$, **42**	416	27	4070	27 ± 1
G_4-729-$[Fe(\eta^5\text{-}C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-$)(\eta^6\text{-}C_6Me_6)][PF_6]$, **43**	416	729	106000	700 ± 40
G_7-19683-$[Fe(\eta^5\text{-}C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-$)(\eta^6\text{-}C_6Me_6)][PF_6]$, **44**	416	19683	2170000	14000 ± 1000
$[Fe(\eta^5\text{-}C_5H_4CO_2CH_2CCH)(\eta^6\text{-}C_6Me_6)][PF_6]$, **37**	413	1	ε_0 = 394	
G_0-9-$[Fe(\eta^5\text{-}C_5H_4CO_2CH_2$-1,2,3-triazolyl-dendr-$)(\eta^6\text{-}C_6Me_6)][PF_6]$, **39**	413	9	3520	9 ± 1
Ionic Bonds				
$[Fe(\eta^5\text{-}C_5H_4CO_2^-PrNH_3^+)(\eta^6\text{-}C_6Me_6)][PF_6]$, **23**	411	1	ε_0 = 321	
G_0-9-$[Fe(\eta^5\text{-}C_5H_4CO_2^-dendrNH_3^+)(\eta^6\text{-}C_6Me_6)][PF_6]$, **24**	411	9	2700	9 ± 1
G_1-27-$[Fe(\eta^5\text{-}C_5H_4CO_2^-dendrNH_3^+)(\eta^6\text{-}C_6Me_6)][PF_6]$, **25**	411	27	8500	27 ± 1
G_2-81-$[Fe(\eta^5\text{-}C_5H_4CO_2^-dendrNH_3^+)(\eta^6\text{-}C_6Me_6)][PF_6]$, **26**	411	81	25800	81 ± 1

Table 5. Hydrodynamic Diameters of the "Clicked" Giant Metallodendrimers Obtained by DLS, and Calculated Diffusion Coefficient, Volume and Density

product[a,b]	MM (g mol^{-1})	hydrodynamic diameter[c] (nm)	diffusion coefficient (m^2 s^{-1})	volume[d] (m^3)	density (kg/m^3)
G_4-FE (**43**)	666 158	26.6 ± 0.5	5.37×10^{-14}	$(9.9 \pm 0.2) \times 10^{-24}$	110 ± 20
G_7-FE (**44**)	18 008913	33.2 ± 1.7	2.93×10^{-14}	$(1.9 \pm 0.4) \times 10^{-23}$	1560 ± 40

[a] G_4-FE (**36**) = G_4-729-$[Fe(\eta^5\text{-}C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-$)(\eta^6\text{-}C_6Me_6)][PF_6]$; G_7-FE (**37**) = G_7-19683-$[Fe(\eta^5\text{-}C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-$)(\eta^6\text{-}C_6Me_6)][PF_6]$. [b] It was not possible to obtain the hydrodynamic diameters of G_0 and G_1 dendrimers by DLS because they are below the lower limit of the technique. [c] Measured in acetone at 25 °C. [d] Considering the globular shape of the dendrimer as a perfect sphere ($V = (4/3)\pi r^3$).

Reduction of C_{60} at −30 °C in situ (MeCN) by **22a** gave an insoluble precipitate that was characterized as the stable complex **45** (Chart 5) by the known EPR signal of $C_{60}^{\bullet -}$[33] (Figure 3) and its Mössbauer spectrum showing the characteristic doublet of the Fe^{II} sandwich complex (Figure 4).[34]

Concluding Remarks

Branching the 18-electron complex $[Fe(\eta^5\text{-}C_5H_4COR)(\eta^6\text{-}C_6Me_6)][PF_6]$ onto the tether termini of large dendrimers was planned to form redox-robust complexes that might ultimately serve as molecular batteries. Various branching modes are presented here. Previous branching via the C_6Me_6 ligand subsequent to C−H activation of this ligand by O_2 in the 19-electron complex **1a** failed because of the insolubility of the small dendritic complexes. Branching via the amino group of the arene ligand in complexes of the type $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5NHR)]$ would not be satisfactory because of the instability of such 19-electron complexes of functional arenes even below room temperature. Branching using the carboxylic acid was still the best choice given the recently reported thermal stability of various 19-electron Fe^I complexes of the type $[Fe^I(\eta^5\text{-}C_5H_4R')(\eta^6\text{-}C_6Me_6)]$ (R′ = carboxylate, ester, thioester, amide) at room temperature.[13c]

Thus, covalent branching via an amido linkage with the Cp ligand has been possible in the present work for various dendrimers up to a theoretical number of 64 groups. It has also been shown here that the bond-lengthening strategy, already used earlier for the synthesis of giant ferrocenyl and cobaltocenyl dendrimers,[16,17] combined with the CuAAC "click" reaction, leads to large organoiron dendrimers with the amido linkage in $[Fe(\eta^5\text{-}C_5H_4CONH\text{-dendr-})(\eta^6\text{-}C_6Me_6)][PF_6]$. The ester linkage was also probed here, and its limit was provided both by the insolubilization of the G_2-81-metallodendrimer and by the decomplexation at ambient temperature of the dendritic Fe^I, 19-electron complexes. This latter feature recalls the decreased thermal stability of the Fe^I, 19-electron complexes $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6R_6)]$ when the length of the alkyl substituents R increases.[35]

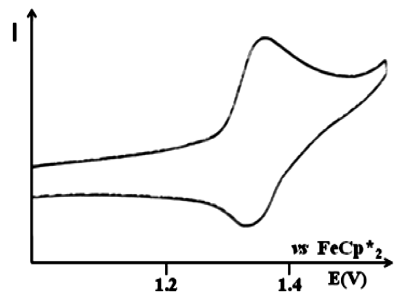

Figure 1. Cyclic voltammogram obtained for G_4-729-$[Fe(\eta^5\text{-}C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-$)(\eta^6\text{-}C_6Me_6)][PF_6]$, **43** in DMF.

Finally, ionic bonding by reactions between the amino-terminated dendrimers and the carboxylic acid was achieved here also with up to 81 organoiron groups. The ionic strategy is limited by the solubility of the dendritic polyamine to 81 terminal branches, because the 243-amino dendrimer is not soluble in THF, unlike the smaller amino-terminated

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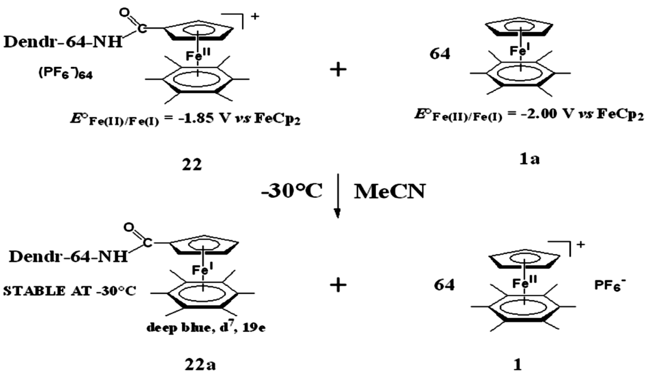
Table 6. Redox Potentials of the Complexes Obtained by CV

complexes	$E_{1/2}$(V)[a]
Ionic Complexes	
G_0-9-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)(η^6-C_6Me_6)]-[PF_6], **24**	−1.680
G_2-81-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)(η^6-C_6Me_6)]-[PF_6], **26**	−1.680
Covalent Complexes	
G_0-9-[Fe(η^5-$C_5H_4CO_2CH_2$-1,2,3-triazolyl-dendr-)-(η^6-C_6Me_6)][PF_6], **39**	−1.220
G_0-9-[Fe(η^5-C_5H_4CONH-)(η^6-C_6Me_6)][PF_6], **19**	−1.360
G_1-27-[Fe(η^5-C_5H_4CONH-)(η^6-C_6Me_6)][PF_6], **20**	−1.360
G_0-9-[Fe(η^5-$C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-)-(η^6-C_6Me_6)][PF_6], **41**	−1.320
G_1-27-[Fe(η^5-$C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-)-(η^6-C_6Me_6)][PF_6], **42**	−1.320
G_4-729-[Fe(η^5-$C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-)-(η^6-C_6Me_6)][PF_6], **43**	−1.320
G_7-19683-[Fe(η^5-$C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-)-(η^6-C_6Me_6)][PF_6], **44**	−1.320

[a] CV recorded at 0.200 V s^{-1}; 20 °C. Solvent: dimethylformamide. Compare [CpFe(η^6-C_6Me_6)][PF_6], **1**, that has an $E_{1/2}$ value of −1.425 V vs Cp_2*Fe in DMF.[4a,12a,12b]

Scheme 5. Reduction $Fe^{II} \rightarrow Fe^{I}$ in the Dendrimer G_4-DAB-64-[Fe(η^5-C_5H_4CONH-)(η^6-C_6Me_6)][PF_6], **22** Using Complex **1a** and Producing the Dendritic 19-Electron Complex G_4-DAB-64-[Fe^I(η^5-C_5H_4-CONH-dendr-)(η^6-C_6Me_6)], **22a**



dendrimers. It is probable that quadruple-ion aggregates are present in these ionic bonds, involving both PF_6^- and carboxylate anions and both iron-centered and ammonium cations.

The strategy involving combination of bond-lengthening and "click" reaction turned out to be the most valuable one, as in the metallocene series. Indeed, it was the only one that could lead to large organoiron dendrimers of this type. All of the strategies are limited to G_1 or G_2 except when the dendritic tethers are lengthened as for the syntheses of large ferrocenyl and cobaltocenyl metallodendrimers. In this case, amido "click" dendrimers could be synthesized up to G_7 with 14 000 ± 1 000 cationic organoiron termini.

Exergonic reduction of the 18-electron Fe^{II} metallodendrimers to 19-electron Fe^{I} metallodendrimers at low temperature is only possible, for solubility reasons, using the classic electron-reservoir complex [Fe^I(η^5-C_5H_5)(η^6-C_6Me_6)], **1a**, as shown with the reduction of the 18-electron metallodendrimer G_4-DAB-64-[Fe^{II}(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)], **22**, in MeCN. The dendritic 19-electron complex **22a** generated in this way serves as a reservoir of approximately 64 electrons to reduce 64 C_{60} molecules to 64 $C_{60}^{\bullet-}$ at −30 °C in acetonitrile.

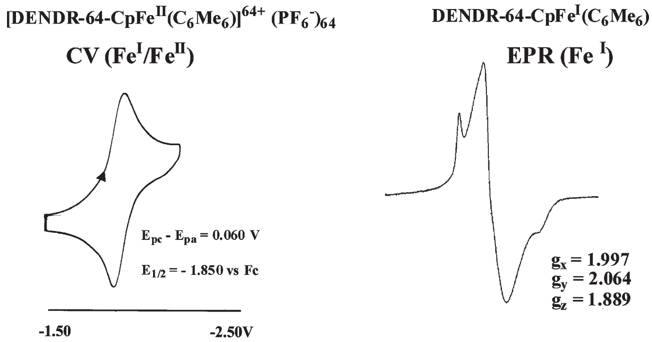


Figure 2. Left: Cyclovoltammogram of the dendritic 18-electron complex G_4-DAB-64-[Fe^{II}(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)], **22** in MeCN, scan rate 0.1 V s^{-1}. Supporting electrolyte: [n-Bu_4N][PF_6]. Reference: ferrocene (Fc). Right: EPR spectrum of the dendritic 19-electron complex G_4-DAB-64-[Fe^I(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)], **22a**, generated as shown in Scheme 5, with 3 g values and rhombic distortion that are characteristic of the Fe^ICp(η^6-arene) family.[12a,18,32].

Experimental Section

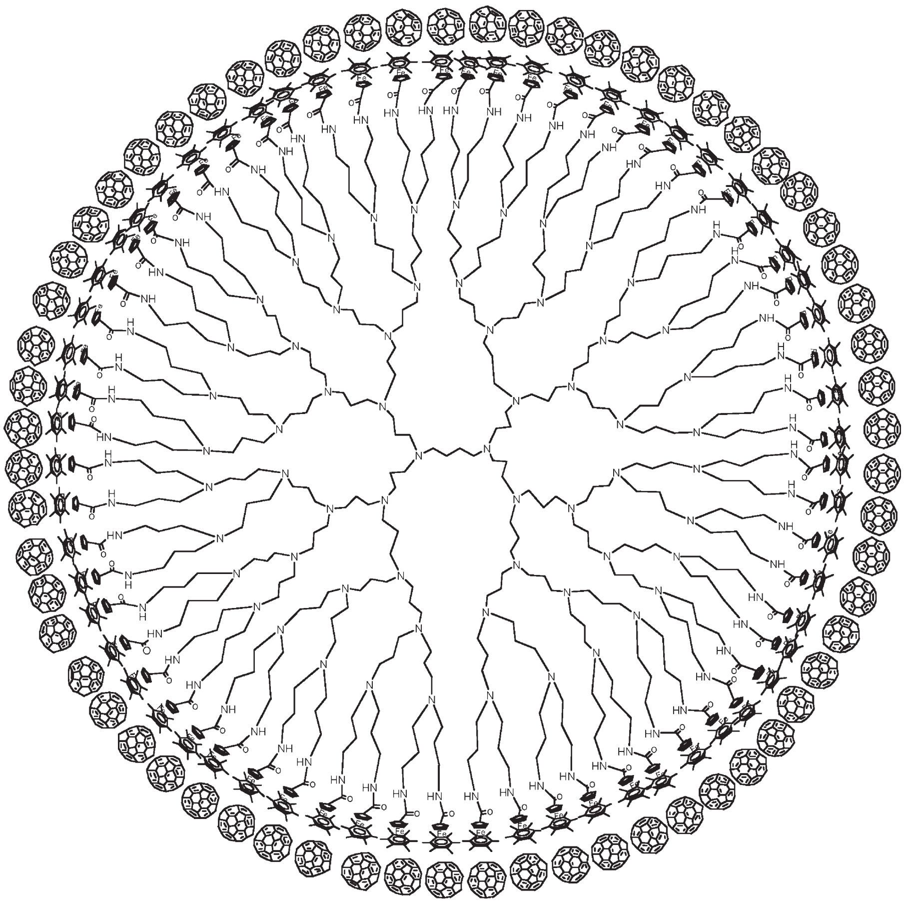
General Data. For general data including solvents, apparatuses, compounds, reactions, spectroscopies and CV, see the Supporting Information. G_n indicates the generation number n. The mononuclear complexes [Fe(η^5-$C_5H_4CO_2H$)(η^6-C_6Me_6)]-[PF_6], **2**, and [Fe(η^5-C_5H_4COCl)(η^6-C_6Me_6)][PF_6], **3**, were synthesized according to ref 13c.

General Synthesis of Amine Dendrimers. A suspension of $LiAlH_4$ (1.5 equiv per branch) in 20 mL of THF cooled at 0 °C under nitrogen, was added dropwise to a solution of azido-terminated dendrimer in 10 mL of THF, that was also cooled at 0 °C under nitrogen. The reaction mixture was stirred for 6 h at 0−8 °C under nitrogen. After slow, cautious addition of H_2O (9 equiv per branch), the gray mixture was stirred at 0 °C for 20 min and filtered over a pad of Celite under nitrogen. The solvent was removed, yielding a colorless solid.

G_0-9-NH_2, 14. The nona-amine dendrimer **14** was synthesized from G_0-9-N_3 (0.100 g, 0.066 mmol), $LiAlH_4$ (0.034 g, 0.89 mmol) and H_2O (0.096 mL, 5.34 mmol) using the general procedure for the synthesis of amino dendrimers. The product was obtained as a white solid (0.068 g, 81% yield). ^{1}H NMR (CD_3CN, 200 MHz), δ_{ppm}: 7.07 (s, 3H, CH core), 2.13 (s, 18H, SiC$H_2$$NH_2$), 1.70 (m, 18H, C_qC$H_2$$CH_2CH_2$Si), 1.47 (s, 18H, $SiCH_2$NH_2), 1.16 (m, 18H, C_qCH_2C$H_2$$CH_2$Si), 0.55 (m, 18H, C_qC$H_2$$CH_2CH_2$Si), 0.00 (s, 54H, Si(C$H_3$)$_2$$CH_2NH_2$). ^{13}C NMR ($CD_3CN$, 50 MHz), δ_{ppm}: 145.7 (C_q of arom. core), 121.6 (CH of arom. core), 43.7 ($C_q$$C$$H_2CH_2CH_2$Si), 41.9 ($C_q$$CH_2CH_2CH_2$Si), 29.9 (Si$(CH_3)_2$$C$$H_2NH_2$), 17.8 ($C_qCH_2$$C$$H_2CH_2$Si), 14.4 ($C_q$-$CH_2CH_2$$C$$H_2$Si), −5.0 (Si($C$$H_3$)$_2CH_2NH_2$). Anal. Calcd for $C_{63}H_{147}Si_9N_9$: C 58.90, H 11.45; found: C 57.97, H 11.37.

G_1-27-NH_2, 15. The 27-arm amine dendrimer **15** was synthesized from G_1-27-N_3 (0.31 g, 0.049 mmol), $LiAlH_4$ (0.075 g, 1.97 mmol), and H_2O (0.02 mL, 2.82 mmol) using the general procedure for the synthesis of amine dendrimers. The product was obtained as a colorless solid (0.214 g, 79% yield). ^{1}H NMR ($CDCl_3$, 200 MHz), δ_{ppm}: 7.22 (d, 18H, arom.), 6.86 (d, 18H, arom.), 7.07 (s, 3H, CH core), 3.54 (s, 18H, SiCH_2O), 2.14 (s, 54H, SiC$H_2$$NH_2$), 1.62 (m, 72H, C_qC$H_2$$CH_2CH_2$Si), 1.13 (m, 72H, C_qCH_2C$H_2$$CH_2$Si), 0.50 (m, 72H, C_qC$H_2$$CH_2CH_2$Si), 0.01 (s, 216H, Si(C$H_3$)$_2$$CH_2NH_2$). ^{13}C NMR ($CDCl_3$, 50 MHz), δ_{ppm}: 159.3 (arom. OC_q), 139.7 (arom. C_q), 127.4 and 113.7 (arom. CH of dendron), 60.4 (Si$C$$H_2$O), 43.3 ($C_q$$C$$H_2CH_2$-$CH_2$Si), 42.4 ($C_q$$CH_2CH_2CH_2$Si), 30.6 (Si$(CH_3)_2$$C$$H_2NH_2$), 18.0 ($C_qCH_2$$C$$H_2CH_2$Si), 14.9 ($C_qCH_2CH_2$$C$$H_2$Si), −4.2 (Si-($C$$H_3$)$_2CH_2NH_2$). Anal. Calcd for $C_{963}H_{1947}N_{81}O_{36}Si_{117}$: C 61.78, H 10.67; found: C 60.92, H 10.65.

Chart 5. Dendr-64-NHCOCpFe(C_6Me_6)$^{64+}$, 64 $C_{60}^{\bullet-}$, **45**, Resulting from the Reaction of **22a** with C_{60} in MeCN/Toluene at −30°C



G_2-81-NH_2, 16. The 81-arm amine dendrimer **16** was synthesized from G_2-81-N_3 (0.100 g, 0.004 mmol), $LiAlH_4$ (0.018 g, 0.47 mmol), and H_2O (0.050 mL, 2.82 mmol) using the general procedure for the synthesis of amino-dendrimers. The product was obtained as a colorless solid (0.051 g, 63% yield). ^{1}H NMR ($CDCl_3$, 200 MHz), δ_{ppm}: 7.15 (d, 72H, arom.), 6.86 (d, 72H, arom.), 7.07 (s, 3H, C*H* core), 3.53 (s, 72H, SiCH_2O), 2.14 (s, 162H, SiC$H_2$$NH_2$), 1.63 (m, 234H, C_qC$H_2$$CH_2$$CH_2$Si), 1.10 (m, 234H, $C_q$$CH_2CH_2$$CH_2$Si), 0.50 (s, 234H, C_qC$H_2$$CH_2CH_2$Si), 0.00 (s, 702H, Si(C$H_3$)$_2$$CH_2$$NH_2$). ^{13}C NMR ($CDCl_3$, 50 MHz), δ_{ppm}: 159.0 (arom. OC_q), 139.2 (arom. C_q), 127.2 and 113.4 (arom. CH of dendron), 60.1 (Si$C$$H_2$O), 42.9 ($C_q$$C$$H_2$$CH_2$$CH_2$Si), 42.1 ($C_q$$CH_2$$CH_2$$CH_2$Si), 30.2 (Si($CH_3$)$_2$$C$$H_2$$NH_2$), 17.7 ($C_q$$CH_2$$C$$H_2$$CH_2$Si), 14.6 ($C_q$$CH_2$$CH_2$$C$$H_2$Si), −4.3 (Si-($C$$H_3$)$_2$$CH_2$$NH_2$). Anal. Calcd for $C_{963}H_{1947}N_{81}O_{36}Si_{117}$: C 62.50, H 10.53; found: C 62.19, H 10.27.

General Synthesis of Metallocene Amido Dendrimers G_n-(3^{n+2})-[Fe(η^5-C_5H_4CONH-)(η^6-C_6Me_6)][PF_6], (n=0−2). A suspension of **2** was heated in refluxing $SOCl_2$ (40 mL) for 16 h, and a homogeneous red solution was obtained. $SOCl_2$ was removed using a trap-to-trap system under nitrogen atmosphere, and [Fe(η^5-C_5H_4COCl)(η^6-C_6Me_6)][PF_6], **3**, was obtained as a red powder.[13c] Then, the complex **3** (1.5 equiv per branch) was dissolved in dry dichloromethane and slowly added to a dichloromethane solution of amino dendrimer and triethylamine (10 equiv per branch). The mixture was stirred under nitrogen atmosphere for 12 h at room temperature. The solvent was removed under vacuum, and the solid residue was dissolved in dichloromethane and washed with an aqueous solution of K_2CO_3, then with an aqueous solution of HPF_6. The organic solution was dried over sodium sulfate, filtered, and removed under vacuum. The product was precipitated with dichloromethane/ether. The product was obtained as an orange powder.

G_0-9-[Fe(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)][PF_6], 19. The metallodendrimer **19** was synthesized from **14** (0.50 g; 0.039 mmol), **2** (0.248 g; 0.526 mmol), $SOCl_2$ (40 mL), and triethylamine (0.354 g, 3.50 mmol) using the general procedure for the synthesis of the metallocene amido dendrimers G_n-(3^{n+2})-[Fe-(η^5-C_5H_4CONH-)(η^6-C_6Me_6)][PF_6], (n=0, 2). The product was obtained as a dark orange solid (0.150 g, 71% yield). ^{1}H NMR (CD_3CN, 200 MHz), δ_{ppm}: 7.02 (s, 3H, C*H* core), 6.74 (s, 9H, CpCON*H*CH_2Si), 4.90 (s, 18H, Cp), 4.68 (s, 18H, Cp), 2.93 (s, 18H, CpCONHCH_2Si), 2.42 (s, 162H, CH_3Ar), 1.66 (m, 18H, C_qC$H_2$$CH_2$$CH_2$Si), 1.14 (m, 18H, $C_q$$CH_2CH_2$$CH_2$Si), 0.57 (m, 18H, C_qC$H_2$$CH_2CH_2$Si), 0.04 (s, 54H, Si(C$H_3$)$_2$$CH_2$$NH_2$). ^{13}C NMR ($CD_3CN$, 50 MHz), δ_{ppm}: 162.1 (C_q=O), 145.7 (C_q of arom. core), 126.9 (CH of arom. core), 99.2 (Cq of C_6Me_6), 84.2 (Cq of Cp), 79.6 and 75.7 (CH of Cp), 43.6 ($C_q$$C$$H_2$$CH_2$$CH_2$Si), 41.5 ($C_q$$CH_2$$CH_2$$CH_2$Si), 29.4 (Si($CH_3$)$_2$$C$$H_2$$NH_2$), 17.5 ($C_q$$CH_2$$C$$H_2$$CH_2$Si), 16.0 ($C$H3Ar), 14.7 ($C_q$$CH_2$$CH_2$$C$$H_2$Si), −4.4 (Si($C$$H_3$)$_2$$CH_2$$NH_2$). Anal. Calcd for $C_{225}H_{336}N_9O_9$-$Si_9P_9F_{54}$: C 55.52, H 6.90; found: C 54.23, H 6.91. IR $\nu_{c=o}$: 1653 cm^{-1}.

G_1-27-[Fe(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)][PF_6], 20. The complex **20** was synthesized from **15** (0.50 g, 0.009 mmol), **2** (0.171 g, 0.362 mmol), $SOCl_2$ (40 mL), and triethylamine (0.244 g, 2.413 mmol) using the general procedure for the synthesis of the amido metallodendrimers G_n-(3^{n+2})-[Fe(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)][PF_6], (n = 0, 2). The product was obtained as a dark orange solid (0.090 g, 58% yield). ^{1}H NMR (CD_3CN, 200 MHz), δ_{ppm}: 7.20 and 6.86 (d, 36H, arom.), 6.71 (s, 27H, SiCH_2N*H*CO), 4.90 (s, 54H, Cp), 4.67 (s, 18H, Cp), 3.57 (s, 18H, SiCH_2O), 2.90 (d, 54H, CpCONHCH_2Si), 2.40 (s, 486H, CH_3Ar), 1.66 (m, 72H, C_qC$H_2$$CH_2$$CH_2$Si), 1.18 (m, 72H, $C_q$$CH_2CH_2$$CH_2$Si), 0.59 (m, 72H, C_qC$H_2$$CH_2CH_2$Si), 0.05 (s, 216H, Si(C$H_3$)$_2$$CH_2$$NH_2$). ^{13}C NMR ($CD_3CN$, 50 MHz),

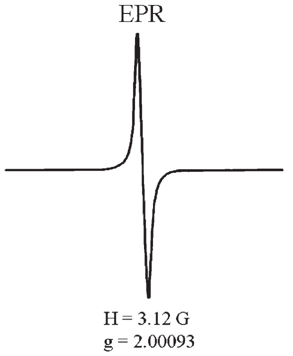


Figure 3. EPR spectrum of **45** in frozen MeCN at 10 K displaying the C60$^{\bullet-}$ signal.[32].

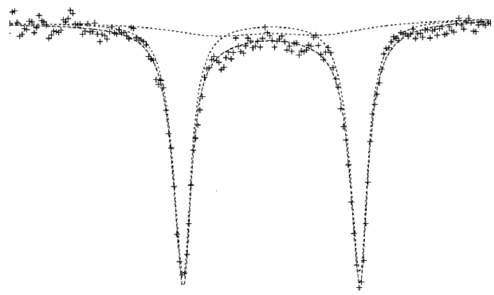


Figure 4. Mössbauer spectrum of **45** displaying the simple quadrupole doublet characteristic of the Fe^{II} center of the **1**$^+$ salts.

δ_{ppm}: 162.3 (C_q=O), 158.9 (arom. C_qO), 139.0 (arom. Cq of dendron), 131.7 and 127.2 (arom. CH of dendron), 99.3 (Cq of C_6Me_6), 84.3 (Cq of Cp), 79.8 and 75.9 (CH of Cp), 60.2 (SiCH_2O), 42.8 (C_q*C*$H_2CH_2CH_2$Si), 41.4 (*C*$_q$$CH_2CH_2CH_2$Si), 29.4 (Si$(CH_3)_2$*C*$H_2NH_2$), 17.6 ($C_qCH_2$*C*$H_2CH_2$Si), 16.2 (*C*$H_3$-Ar), 14.7 ($C_qCH_2CH_2$*C*$H_2$Si), −4.4 (Si(*C*$H_3)_2CH_2NH_2$). Anal. Calcd for $C_{774}H_{1164}N_{27}O_{36}Si_{36}P_{27}F_{162}$: C 55.52, H 6.90; found: C 55.38, H 6.86. IR $\nu_{c=o}$: 1657 cm^{-1}.

G$_4$-DAB-64-{[Fe^{II}(η^5-C$_5$H$_4$CONH-dendr)(η^6-C$_6$Me$_6$)][PF$_6$]}, 22. The dendrimer DAB-*dendr*-$(NH_2)_{64}$ **21** (0.080 g, 0.0112 mmol) and triethylamine (0.156 mL, 1.07 mmol) were dissolved in 20 mL of dry CH_2Cl_2. A solution of **3**, (0.500 g, 1.07 mmol) in 40 mL of CH_3CN was added dropwise to this mixture. The solution was stirred at room temperature overnight, then the solvent was removed under vacuum, the solid residue was washed twice with saturated sodium carbonate solution and twice with water, dissolved in CH_3CN and dried over sodium sulfate. After filtration, the volume was reduced to 5 mL, and precipitation from this solution with 50 mL of dry CH_2Cl_2 gave the dendrimer **22** as a brown powder (0.101 g, 25% yield). ^{1}H NMR (CD_3CN, 200 MHz), δ_{ppm}: 7.69 (br, 64H, NH); 4.9 (br. 128H, C_5H_4); 4.6 (br. 128H, C_5H_4) ; 3.3 (br. 124H, NH$\underline{CH_2}$); 2.3 (br. 1152H, CH_3 and 372H, CH_2HNCH_2); 1.69 and 1.49 (br. 252H, CH_2CH_2N). ^{13}C NMR (CD_3CN, 50 MHz), δ_{ppm}: 162.7(C═O); 99.2 (C_q, $\underline{C}_6Me_6$); 83.6 (C_q, C_5H_4); 79.6; 75.7 (CH, C_5H_4); 51.4 ($CH_2N\underline{CH_2}$); 38.2 ($NHCH_2$); 26.5 ($CH_2\underline{CH_2}CH_3$); 15.9 (CH_3). IR (nujol, cm^{-1}): 3422 (ν_{NH}), 1649 ($\nu_{C=O}$), 1532 ($\nu_{O=CNH}$), 840 (PF_6). Anal. Calcd. for $C_{1528}H_{2224}NOFe_{64}P_{64}F_{384}$: C 50.65, H 6.17; found: C 48.73; H 6.23. $E_{1/2}$ (V vs FeCp*$_2$, DMF, 20 °C): −1.370 V.

General Synthesis of [Fe(η^5-C$_5$H$_4$CO$_2^-$NH$_3^+$Pr)(η^6-C$_6$Me$_6$)]-[PF$_6$], 23, and G$_n$-(3^{n+2})-[Fe(η^5-C$_5$H$_4$CO$_2^-$NH$_3^+$dendr)(η^6-C$_6$-Me$_6$)][PF$_6$], (n = 0−2), 24−26. The complex **2** (1 equiv per amine group) in 5 mL of acetonitrile was added dropwise at ambient temperature under nitrogen to a solution of amino dendrimer in 5 mL of acetonitrile. After 5 min of agitation, the solvent was evaporated, and an orange powder was obtained.

[Fe(η^5-C$_5$H$_4$CO$_2^-$PrNH$_3^+$)(η^6-C$_6$Me$_6$)][PF$_6$], 23. The complex **23** was synthesized from propylamine (0.025 g, 0.43 mmol) and **2** (0.200 g, 0.423 mmol) using the above general procedure for the synthesis of [Fe(η^5-C$_5$H$_4$CO$_2^-$NH$_3^+$Pr)(η^6-C$_6$Me$_6$)]-[PF$_6$] and G$_n$-(3^{n+2})-[Fe(η^5-C$_5$H$_4$CO$_2^-$NH$_3^+$dendr)(η^6-C$_6$Me$_6$)]-[PF$_6$]. The product **23** was obtained as an orange powder (0.221 g; 99% yield). ^{1}H NMR (CD_3CN, 200 MHz), δ_{ppm}: 4.73 and 4.55 (s, 4H, Cp), 2.97 (t, 2H, $^+NH_3$*C*$H_2CH_2CH_3$), 2.44 (s, 18H, C_6Me_6), 1.78 (m, 2H, $^+NH_3CH_2$*C*H_2CH_3), 1.06 (t, 2H, $^+NH_3CH_2CH_2$-*C*H_3). ^{13}C NMR (CD_3CN, 50 MHz), δ_{ppm}: 168.1 (C═O), 98.6 (*C*$_6Me_6$), 88.3 (Cq of Cp), 79.3 and 78.3 (CH of Cp), 16.0 (CH_3 of C_6Me_6). Anal. Calcd for $C_{21}H_{32}NO_2FePF_6$: C 47.45, H 6.02; found: C 46.62, H 5.80

G$_0$-9-[Fe(η^5-C$_5$H$_4$CO$_2^-$dendrNH$_3^+$)(η^6-C$_6$Me$_6$)][PF$_6$], 24. The complex **24** was synthesized from **14** (0.025 g, 0.020 mmol) and **2** (0.083 g, 0.175 mmol) using the above general procedure for the synthesis of G$_n$-(3^{n+2})-[Fe(η^5-C$_5$H$_4$CO$_2^-$NH$_3^+$dendr)(η^6-C$_6$-Me$_6$)][PF$_6$]. The product was obtained as an orange powder (0.106 g, 99% yield). ^{1}H NMR (CD_3CN, 200 MHz), δ_{ppm}: 6.95 (s, 3H, *CH* core), 4.73 and 4.58 (s, 36H, Cp), 2.42 (m, 162H of C_6Me_6 and 18H of Si*C*$H_2NH_3^+$), 1.60 (s, 18H, C_q*C*$H_2CH_2CH_2$Si), 1.08 (s, 18H, C_qCH_2*C*H_2CH_2Si), 0.65 (s, 18H, C_q*C*H_2CH_2*C*H_2Si), 0.15 (s, 54H, Si(*C*$H_3)_2CH_2NH_3^+$). ^{13}C NMR (CD_3CN, 50 MHz), δ_{ppm}: 167.9 (C═O), 145.5 (C_q of arom. core), 121.5 (CH of arom. core), 98.7, (Cq of C_6Me_6), 87.4 (Cq of Cp), 79.5 and 78.2 (CH of Cp), 43.6 (C_q*C*$H_2CH_2CH_2$Si), 41.5 (*C*$_q$$CH_2CH_2CH_2$Si), 27.1 (Si$(CH_3)_2$*C*$H_2NH_3^+$), 17.5 ($C_qCH_2$*C*$H_2CH_2$Si), 15.9 ($CH_3$ of C_6Me_6), 14.3 ($C_qCH_2CH_2$*C*H_2Si), −4.5 (Si(*C*$H_3)_2CH_2NH_3^+$). Anal. Calcd for $C_{225}H_{354}N_9O_{18}Si_9Fe_9P_9F_{54}$: C 48.83, H 6.40; found: C 48.04, H 6.50.

G$_1$-27-[Fe(η^5-C$_5$H$_4$CO$_2^-$dendrNH$_3^+$)(η^6-C$_6$Me$_6$)][PF$_6$], 25. The complex **25** was synthesized from **15** (0.025 g, 0.005 mmol) and **2** (0.057 g, 0.121 mmol) using the above general procedure for the synthesis of G$_n$-(3^{n+2})-[Fe(η^5-C$_5$H$_4$CO$_2^-$NH$_3^+$dendr)-(η^6-C$_6$Me$_6$)][PF$_6$]. The product was obtained as an orange powder (0.073 g, 89% yield). ^{1}H NMR CD_3CN, 200 MHz), δ_{ppm}: 7.14 (d, 18H, arom.), 6.80 (d, 18H, arom.), 4.76 and 4.58 (s, 108H, Cp), 3.48 (s, 18H, Si*C*H_2O), 2.41 (m, 486H of C_6Me_6 and 54H of Si*C*$H_2NH_3^+$), 1.64 (m, 72H, C_q*C*$H_2CH_2CH_2$Si), 1.12 (m, 72H, C_qCH_2*C*H_2CH_2Si), 0.64 (m, 72H, $C_qCH_2CH_2$*C*H_2Si), 0.14 (s, 216H, Si(*C*$H_3)_2CH_2NH_2$). ^{13}C NMR (CD_3CN, 50 MHz), δ_{ppm}: 167.6 (C═O), 158.9 (arom. OC_q), 139.3 (arom. C_q), 127.2 and 113.2 (arom. CH of dendron), 98.8 (Cq of C_6Me_6), 86.1 (Cq of Cp), 79.6 and 78.2 (CH of Cp), 60.3 (Si*C*H_2O), 42.8 (C_q*C*$H_2CH_2CH_2$Si), 41.4 (*C*$_q$$CH_2CH_2CH_2$Si), 27.2 (Si$(CH_3)_2$*C*$H_2NH_3^+$), 17.3 ($C_qCH_2$*C*$H_2CH_2$Si), 16.1 ($CH_3$ of C_6Me_6), 14.3 ($C_qCH_2CH_2$*C*H_2Si), −4.7 (Si(*C*$H_3)_2CH_2NH_3^+$). Anal. Calcd for $C_{774}H_{1218}N_{27}O_{63}Si_{36}Fe_{27}P_{27}F_{162}$: C 50.67, H 6.64; found: C 50.41, H 6.58.

G$_2$-81-[Fe(η^5-C$_5$H$_4$CO$_2^-$dendrNH$_3^+$)(η^6-C$_6$Me$_6$)][PF$_6$], 26. The complex **26** was synthesized from **16** (0.025 g, 0.0014 mmol) and **2** (0.052 g, 0.110 mmol) using the above general procedure for the synthesis of G$_n$-(3^{n+2})-[Fe(η^5-C$_5$H$_4$CO$_2^-$NH$_3^+$dendr)-(η^6-C$_6$Me$_6$)][PF$_6$]. The product was obtained as an orange powder (0.072 g; 93% yield). ^{1}H NMR CD_3CN, 200 MHz), δ_{ppm}: 7.20 (d, 72H, arom.), 6.84 (d, 72H, arom.), 4.77 and 4.58 (s, 324H, Cp), 3.51 (s, 72H, Si*C*H_2O), 2.43 (m, 1458 H of C_6Me_6 and 162H of Si*C*$H_2NH_3^+$), 1.67 (m, 243H, C_q*C*$H_2CH_2CH_2$Si), 1.13 (m, 243H, C_qCH_2*C*H_2CH_2Si), 0.66 (m, 243H, $C_qCH_2CH_2$-*C*H_2Si), 0.16 (s, 702H, Si(*C*$H_3)_2CH_2NH_2$). ^{13}C NMR (CD_3CN, 50 MHz), δ_{ppm}: 167.4 (C═O), 158.9 (arom. OC_q), 139.0 (arom. C_q), 127.2 and 113.2 (arom. CH of dendron), 98.9 (Cq of C_6Me_6), 85.0 (Cq of Cp), 79.8 and 78.2 (CH of Cp), 60.1 (Si*C*H_2O), 42.9 (C_q*C*$H_2CH_2CH_2$Si), 41.5 (*C*$_q$$CH_2CH_2CH_2$Si), 27.0 (Si$(CH_3)_2$*C*$H_2NH_3^+$), 17.2 ($C_qCH_2$*C*$H_2CH_2$Si), 16.1 ($CH_3$ of C_6Me_6), 14.1 ($C_qCH_2CH_2$*C*H_2Si), −4.5 (Si(*C*$H_3)_2CH_2NH_3^+$). Anal. Calcd for $C_{2421}H_{3810}N_{81}O_{198}Si_{117}Fe_{81}P_{81}F_{486}$: C 51.18, H 6.71; found: C 49.21, H 6.58.

[Fe(η^5-C$_5$H$_4$CO$_2^-$Na$^+$)Cp], 27a. To a solution of NaOH (0.087 g, 0.217 mmol) in 5 mL of EtOH, was added **27** at ambient temperature. After stirring for 5 min, the solvent was removed under vacuum, and the product **27a** was obtained as an orange powder (0.080 g, 98% yield). ^{1}H NMR (D_2O, 200 MHz), δ_{ppm}: 4.59 and 4.36 (s, 4H, Cp), 4.19 (s, 5H, Cp). ^{13}C NMR (D_2O, 200 MHz), δ_{ppm}: 180 (C=O), 76.3 (Cq of Cp), 70.7 and 70.0 (CH of Cp), 69.6 (*C*H of Cp).

General Synthesis of Ferrocene Carboxylate Propylammonium, 28, and Polyammoniums 29−31. The complex **27** (1 equiv per branch or 1 equiv for propylamine) in 5 mL of THF was added dropwise at ambient temperature to a 5 mL-THF solution of amino-dendrimer at ambient temperature under nitrogen. A precipitate formed, and the solvent was evaporated, giving an orange powder.

[Fe(η^5-$C_5H_4CO_2^-$PrNH_3^+)Cp], 28. The complex **28** was synthesized from propylamine (0.025 g, 0.423 mmol) and **27** (0.097 g, 0.423 mmol) using the general procedure for synthesis of G_n-(3^{n+2})-[Fe(η^5-$C_5H_4CO_2^-NH_3^+$dendr)(η^6-C_6Me_6)][PF_6]. The product was obtained as an orange powder (0.121 g, 99% yield). ^{1}H NMR (D_2O, 200 MHz), δ_{ppm}: 4.60 and 4.37 (s, 4H, Cp), 4.20 (s, 5H, Cp), 2.90 (t, 2H, $^+NH_3CH_2CH_2CH_3$), 1.61 (m, 2H, $^+NH_3CH_2CH_2CH_3$), 0.91 (t, 3H, $^+NH_3CH_2CH_2CH_3$). ^{13}C NMR (D_2O, 50 MHz) δ_{ppm}: 159.8 (C=O), 76.3 (Cq of Cp), 70.7 and 70.0 (CH of Cp), 69.5 (Cp), 40.9 ($^+NH_3CH_2CH_2CH_3$), 20.1 ($^+NH_3CH_2CH_2CH_3$), 9.9 ($^+NH_3CH_2CH_2CH_3$). Anal. Calcd for $C_{14}H_{19}NO_2Fe$: C 58.13, H 6.57; found: C 57.97, H 6.53.

G_0-9-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)Cp], 29. The metallodendrimer **29** was synthesized from **14** (0.025 g, 0.020 mmol) and **27** (0.040 g, 0.175 mmol) using the general procedure for synthesis of ferrocenylcarboxylate ammonium dendrimers or propylammonium. The product was obtained as an orange powder (0.060 g; 92% yield). ^{1}H NMR (CD_3CN, 200 MHz), δ_{ppm}: 7.10 (s, 3H, *C*H core), 4.73 and 4.36 (s, 36H, Cp), 4.19 (s, 45H, Cp), 2.02 (s, 162H, Si$CH_2NH_3^+$), 1.72 (s, 18H, $C_qCH_2CH_2CH_2Si$), 1.20 (s, 18H, $C_qCH_2CH_2CH_2Si$), 0.56 (s, 18H, $C_qCH_2CH_2CH_2Si$), 0.00 (s, 54H, Si$(CH_3)_2CH_2NH_2$). Anal. Calcd for $C_{162}H_{237}N_9O_{18}Si_9Fe_9$: C 58.01, H 7.07; found: C 57.56, H 7.05.

G_1-27-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)Cp], 30. The metallodendrimer **30** was synthesized from **15** (0.025 g, 0.0013 mmol) and **27** (0.024 g, 0.103 mmol) using the general procedure for synthesis of ferrocenylcarboxylate ammonium dendrimers. The product was obtained as an orange powder (0.045 g, yield: 93%). ^{1}H NMR $(CD_3)_2CO$, 200 MHz), δ_{ppm}: 7.21 (d, 18H, CH arom.), 6.90 (d, 18H, CH arom.), 4.73 and 4.42 (s, 108H, Cp), 4.19 (s, 135H, Cp), 3.57 (s, 18H, SiCH_2O), 2.03 (s, 54H, Si$CH_2NH_3^+$), 1.71 (m, 72H, $C_qCH_2CH_2CH_2Si$), 1.18 (m, 72H, $C_qCH_2CH_2CH_2Si$), 0.52 (m, 72H, $C_qCH_2CH_2CH_2Si$), 0.00 (s, 216H, Si$(CH_3)_2CH_2N$). Anal. Calcd for $C_{585}H_{867}N_{27}O_{63}Si_{36}Fe_{27}$: C 59.54, H 7.35; found: C 59.53, H 7.37

G_2-81-[Fe(η^5-$C_5H_4CO_2^-$dendrNH_3^+)Cp], 31. The metallodendrimer **31** was synthesized from **16** (0.027 g, 0.0014 mmol) and **27** (0.026 g, 0.117 mmol) using the general procedure for the synthesis of the ferrocenylcarboxylate ammonium dendrimers. The product **22** was obtained as an orange powder (0.050 g, 94% yield). ^{1}H NMR ($(CD_3)_2CO$, 200 MHz), δ_{ppm}: 7.23 (d, 72H, CH arom.), 6.87 (d, 72H, CH arom.), 4.73 and 4.39 (s, 324H, Cp), 4.19 (s, 405H, Cp), 3.55 (s, 72H, SiCH_2O), 2.03 (s, 162H, Si$CH_2NH_3^+$), 1.69 (m, 234H, $C_qCH_2CH_2CH_2Si$), 1.19 (m, 234H, $C_qCH_2CH_2CH_2Si$), 0.52 (m, 234H, $C_qCH_2CH_2CH_2Si$), 0.00 (s, Si$(CH_3)_2CH_2N$). Anal. Calcd for $C_{1854}H_{2757}N_{81}O_{138}Si_{36}Fe_{81}$: C 59.93, H 7.42; found: C 59.05 H 7.77.

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

General Procedure for the Synthesis of Azido Dendrimers. The chloromethyl-terminated dendrimers and NaN_3 (2 equiv per branch) were introduced into a Schlenk flask, then dry DMF (30 mL) was added. The reaction mixture was heated at 80 °C for 12 h under magnetic stirring. After removing the solvent in vacuo, dichloromethane was added, and the mixture was filtered through Celite. The solvent was removed in vacuo, and the residue was washed with methanol (2 × 10 mL) and precipitated from a CH_2Cl_2 solution by addition of MeOH. After drying in vacuo, the azido dendrimers were obtained as colorless products.

Synthesis of (11-Bromoundecyl)dimethylsilane, 32. (i) 11-Bromo-1-undecene (4.29 g, 18.4 mmol), dimethylchlorosilane (3.48 g, 36.8 mmol), dry ethylic ether, and 12 drops of Kartstedt catalyst were successively introduced in a Schlenk flask. The reaction mixture was stirred under nitrogen atmosphere at room temperature for 16 h. The solvent and excess of dimethylchlorosilane were removed under vacuum, giving (11-bromoundecyl)-chlorodimethylsilane (18.4 mmol) as a colorless oil. (ii) (11-Bromoundecyl)chlorodimethylsilane (18.4 mmol) was dissolved in dry ether and slowly added to a suspension of $LiAlH_4$ (6 g) in dry ether. The mixture was heated at 55 °C for 2 h. The solution was cooled at 0 °C, and an aqueous solution of HCl (35%) was added dropwise until it reached an acidic pH value. A 300 mL portion of ether and 100 mL of water were added, and the organic phase was extracted and dried over sodium sulfate, filtered, and the solvent was removed under vacuum. The product was purified by flash chromatography using silica gel with ether as the eluent, yielding (11-bromoundecyl)dimethylsilane (3.20 g, 59% yield). ^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 3.31 (m, 2H, CH_2Br), 1.84 (m, 2H, CH_2CH_2Br), 1.27 (m, 16H, $(CH_2)_8$), 0.58 (s, 2H, CH_2Si), 0.049 (s, 6H, Si$(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 62.90 MHz), δ_{ppm}: 34.3 (CH_2CH_2Br), 33.0 (CH_2Br), 29.9 ($(CH_2)_8$), 10.5 (CH_2Si), −6.7 (Si$(CH_3)_2$). Anal. Calcd for $C_{13}H_{29}$SiBr: C 53.23, H 9.96; found: C 53.11, H 9.87.

Synthesis of G_0-long-N_3, 33. (i) Hydrosilylation of G_0-9-allyl **4** (0.050 g, 0.104 mmol) using the silane **32** (0.549 g, 1.87 mmol) was carried out using the general procedure for the hydrosilylation reactions giving G_0-long-Br as a colorless waxy product (0.323 g, 99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 6.93 (s, 3H, *C*H core), 3.40 (m, 18H, CH_2Br), 1.84 (m, 18H, CH_2CH_2Br), 1.57 (s, 18H, $C_qCH_2CH_2CH_2Si$), 1.26 (m, 144H, $(CH_2)_8$), 1.04 (s, 18H, $C_qCH_2CH_2CH_2Si$), 0.42 (s, 36H, CH_2SiCH_2), −0.10 (s, 54H, Si$(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 62.90 MHz), δ_{ppm}: 145.7 (C_q of arom. core), 121.5 (*C*H of arom. core), 43.9 ($C_qCH_2CH_2CH_2Si$), 42.2 (benzylic C_q), 33.8 (CH_2CH_2Br), 32.8 (CH_2Br), 29.5 ($(CH_2)_7$), 24.0 (CH_2CH_2Si), 18.0 ($C_qCH_2CH_2CH_2Si$), 16.3 (CH_2Si), 15.6 ($C_qCH_2CH_2CH_2Si$), −3.1 (Si$(CH_3)_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: 2.11 (*Si*(Me)$_2$). Mass spectrum (MALDI-TOF; *m*/*z*), calcd. for $C_{153}H_{309}Si_9Br_9Na$ (MNa^+): 3 144.04, found: 3 144.44. Anal. Calcd for $C_{153}H_{309}Si_9Br_9$: C 58.88, H 9.98; found: C 59.63, H 10.24. (ii) The dendrimer **33** was synthesized from G_0-long-Br (0.120 g, 0.0385 mmol) and NaN_3 (0.045 g, 0.693 mmol) using the general procedure for the synthesis of azido dendrimers, giving **33** as a colorless waxy product (0.106 g, 99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 6.93 (s, 3H, *C*H core), 3.25 (m, 18H, CH_2N_3), 1.58 (s, 36H, $CH_2CH_2CH_2Si$), 1.26 (m, 180H, $(CH_2)_9$ and $CH_2CH_2CH_2Si$), 0.43 (s, 36H, CH_2SiCH_2), −0.11 (s, 54H, Si$(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 62.90 MHz), δ_{ppm}: 145.8 (C_q of arom. core), 121.5 (*C*H of arom. core), 51.1 (CH_2N_3), 43.8 ($C_qCH_2CH_2CH_2Si$), 42.1 (benzylic C_q), 33.2 ($CH_2CH_2N_3$), 29.5 ($(CH_2)_7$), 23.4 (CH_2CH_2Si), 17.9 ($C_qCH_2CH_2CH_2Si$), 16.3 (CH_2Si), 14.9 ($C_qCH_2CH_2CH_2Si$), −3.3 (Si$(CH_3)_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: 2.11 (*Si*(Me)$_2$). Anal. Calcd for $C_{153}H_{309}Si_9N_{27}$: C 58.88, H 9.98; found: C 59.63, H 10.24. IR υ_{N3}: 2 097 cm^{-1}.

Synthesis of G_1-long-N_3, 34. (i) Hydrosilylation of G_1-27-allyl **7** (0.050 g, 0.0159 mmol) with the silane **32** (0.249 g, 0.85 mmol) was carried out using the general procedure for the hydrosilylation reactions, yielding G_1-27-long-Br as a colorless waxy product (0.174 g, 98% yield). ^{1}H NMR ($CDCl_3$, 300 MHz),

δ_{ppm}: 7.14 (d, 54H, arom), 7.05 (s, 3H, C*H* core), 6.84 (d, 54H, arom), 3.51 (s, 18H, CH_2O), 3.40 (m, 54H, CH_2Br), 1.85 (m, 54H, C$H_2$$CH_2$Br), 1.55 (s, 72 H, C_qC$H_2$$CH_2CH_2$Si), 1.25 (m, 144H, $(CH_2)_9$), 0.41 (s, 108H, CH_2SiCH_2), −0.10 (s, 54H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 62.90 MHz), δ_{ppm}: 158.5 (arom. OC_q), 139.2 (arom. C_q), 126.7 and 112.9 (arom. *C*H of dendron), 59.7 (Si*C*H_2O), 42.6 (C_q*C*$H_2CH_2CH_2$Si), 41.2 (benzylic C_q), 33.3 (*C*H_2CH_2Br), 32.7 (*C*H_2Br), 29.2 ($(CH_2)_7$), 24.1 (*C*H_2CH_2-Si), 17.8 (C_qCH_2*C*H_2CH_2Si), 16.2 (*C*H_2Si), 15.3 ($C_qCH_2CH_2$-*C*H_2Si), −3.6 (Si(*C*H_3)$_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: 2.12 (*Si*(Me)$_2$). Anal. Calcd for $C_{558}H_{1083}O_9Si_{36}Br_{27}$: C 60.35, H 9.83; found: C 59.81, H 9.80. (ii) The dendrimer **34** was synthesized from G_1-long-Br (0.142 g, 0.0128 mmol) and NaN_3 (0.045 g, 0.693 mmol) using the general procedure for the synthesis of the azido dendrimers, giving **34** as a colorless waxy product (0.128 g, 99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 7.15 (d, 54H, arom), 7.05 (s, 3H, C*H* core), 6.84 (d, 54H, arom), 3.51 (s, 18H, CH_2O), 3.23 (m, 54H, CH_2N_3), 1.57 (s, 72 H, C_qC$H_2CH_2CH_2$Si), 1.26 (m, 144H, $(CH_2)_9$), 0.42 (s, 108H, CH_2SiCH_2), −0.10 (s, 54H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 62.90 MHz), δ_{ppm}: 158.4 (arom. OC_q), 139.1 (arom. C_q), 126.7 and 112.9 (arom. *C*H of dendron), 59.7 (Si*C*H_2O), 51.1 (CH_2N_3), 42.6 (C_q*C*$H_2CH_2CH_2$Si), 41.2 (benzylic C_q), 33.3 (*C*$H_2CH_2N_3$), 32.7 (*C*H_2N_3), 29.3 ($(CH_2)_7$), 24.1 (*C*H_2CH_2Si), 17.8 (C_qCH_2*C*H_2CH_2Si), 16.2 (*C*H_2Si), 15.3 ($C_qCH_2CH_2$-*C*H_2Si), −3.6 (Si(*C*H_3)$_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: 2.12 (*Si*(Me)$_2$).

Synthesis of G_4-long-N_3, 35. (i) Hydrosilylation of G_4-729-allyl **10** (0.050 g, 4.60. 10^{-4} mmol) using the silane **32** (0.197 g, 0.0671 mmol) was carried out using the general procedure for the hydrosilylation reactions, giving G_4-729-long-Br as a colorless waxy product (0.142 g, 96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 7.12 (d, arom), 6.82 (d, arom), 3.50 (s, CH_2O), 3.38 (m, CH_2Br), 1.86 (m, CH_2CH_2Br), 1.57 (s, C_qC$H_2CH_2CH_2$Si), 1.25 (m, $(CH_2)_9$), 0.42 (s, CH_2SiCH_2), −0.06 (s, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 62.90 MHz), δ_{ppm}: 158.4 (arom. OC_q), 139.1 (arom. C_q), 126.7 and 112.9 (arom. *C*H of dendron), 59.8 (Si*C*H_2O), 42.6 (C_q*C*$H_2CH_2CH_2$Si), 41.2 (benzylic C_q), 33.3 (*C*H_2CH_2Br), 32.7 (*C*H_2Br), 29.2 ($(CH_2)_7$), 24.1 (*C*H_2CH_2Si), 17.8 (C_qCH_2*C*H_2CH_2Si), 16.1 (*C*H_2Si), 15.2 ($C_qCH_2CH_2$*C*H_2-Si), −3.6 (Si(*C*H_3)$_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: 2.12 (*Si*(Me)$_2$). Anal. Calcd for $C_{16353}H_{31269}O_{360}Si_{1089}Br_{729}$: C 60.90, H 9.77; found: C 59.47, H 9.77. (ii) The dendrimer **34** was synthesized from G_4-long-Br (0.050 g, 0.000155 mmol) and NaN_3 (0.015 g, 0.226 mmol) using the general procedure for the synthesis of the azido dendrimers. The product **34** was obtained as a colorless waxy product (0.045 g, 98% yield). ^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 7.14 (d, arom), 6.84 (d, arom), 3.50 (s, CH_2O), 3.25 (m, CH_2N_3), 1.59 (s, C_qC$H_2CH_2CH_2$Si), 1.28 (m, $(CH_2)_9$), 0.42 (s, CH_2SiCH_2), −0.10 (s, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 62.90 MHz), δ_{ppm}: 158.4 (arom. OC_q), 138.9 (arom. C_q), 126.6 and 112.8 (arom. *C*H of dendron), 59.5 (Si*C*H_2O), 51.2 (CH_2N_3), 42.5 (C_q*C*$H_2CH_2CH_2$Si), 41.2 (benzylic C_q), 33.3 (*C*$H_2CH_2N_3$), 32.7 (*C*H_2N_3), 29.3 ($(CH_2)_7$), 24.1 (*C*H_2CH_2Si), 17.6 (C_qCH_2*C*H_2CH_2Si), 16.3 (*C*H_2Si), 15.3 ($C_qCH_2CH_2$*C*H_2Si), −3.6 (Si(*C*H_3)$_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: 2.12 (*Si*(Me)$_2$).

Synthesis of G_7-long-N_3, 36. (i) Hydrosilylation of G_7-allyl **13** (0.050 g, 1.69. 10^{-5} mmol) with the silane **32** (0.195 g, 0.0666 mmol) was carried out using the general procedure for the hydrosilylation reactions, giving G_7-long-Br as a colorless waxy product (0.134 g, 91% yield). ^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 7.12 (d, arom), 6.78 (d, arom), 3.50 (s, CH_2O), 3.39 (m, CH_2Br), 1.82 (m, CH_2CH_2Br), 1.57 (s, C_qC$H_2CH_2CH_2$Si), 1.26 (m, $(CH_2)_9$), 0.41 (s, CH_2SiCH_2), −0.06 (s, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 62.90 MHz), δ_{ppm}: 158.3 (arom. OC_q), 139.1 (arom. C_q), 126.8 and 112.8 (arom. *C*H of dendron), 59.7 (Si*C*H_2O), 42.7 (C_q*C*$H_2CH_2CH_2$Si), 41.2 (benzylic C_q), 33.4 (*C*H_2CH_2-Br), 32.7 (*C*H_2Br), 29.4 ($(CH_2)_7$), 24.1 (*C*H_2CH_2Si), 17.8 (C_qCH_2*C*H_2CH_2Si), 16.1 (*C*H_2Si), 15.2 ($C_qCH_2CH_2$*C*H_2Si), −3.6 (Si(*C*H_3)$_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: 2.13 (*Si*(Me)$_2$).Anal. Calcd for $C_{442818}H_{846291}O_{9837}Si_{29520}Br_{19683}$: C 60.92, H 9.77; found: C 57.32, H 9.52. (ii) The dendrimer **35** was synthesized from G_7-long-Br (0.050 g, 5.73. 10^{-6} mmol) and NaN_3 (0.015 g, 0.226 mmol) using the general procedure for the synthesis of azido dendrimers, giving **36** as a colorless waxy product (0.043 g, 93% yield). ^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 7.11 (d, arom), 6.78 (d, arom), 3.50 (s, CH_2O), 3.25 (m, CH_2N_3), 1.59 (s, C_qC$H_2CH_2CH_2$Si), 1.25 (m, $(CH_2)_9$), 0.42 (s, CH_2SiCH_2), −0.10 (s, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 62.90 MHz), δ_{ppm}: 158.5 (arom. OC_q), 138.8 (arom. C_q), 126.6 and 112.9 (arom. *C*H of dendron), 59.6 (Si*C*H_2O), 51.2 (CH_2N_3), 42.5 (C_q*C*$H_2CH_2CH_2$Si), 41.2 (benzylic C_q), 33.5 (*C*$H_2CH_2N_3$), 32.9 (*C*H_2N_3), 29.3 ($(CH_2)_7$), 24.1 (*C*H_2CH_2Si), 17.6 (C_qCH_2*C*H_2CH_2Si), 16.3 (*C*H_2Si), 15.3 ($C_qCH_2CH_2$*C*H_2Si), −3.6 (Si(*C*H_3)$_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: 2.12 (*Si*(Me)$_2$).

[Fe(η^5-$C_5H_4CO_2CH_2C{\equiv}CH$)($\eta^6$-$C_6Me_6$)][$PF_6$], 37. A suspension of **2** (2 g, 5.75 mmol) was heated in refluxing $SOCl_2$ (40 mL) for 16 h, giving an homogeneous red solution of **3**. $SOCl_2$ was removed using a trap-to-trap system under nitrogen atmosphere, and the red powder of **3** was dissolved in dry dichloromethane and slowly added to a dichloromethane solution of propargyl alcohol (0.644 g, 11.49 mmol) and triethylamine (3 mL). The mixture was stirred under nitrogen atmosphere for 2 h at room temperature. The solvent was removed under vacuum, dissolved with dichloromethane and washed with an aqueous solution of K_2CO_3 and with an aqueous solution of HPF_6. The organic solution was dried with sodium sulfate, filtered, and the solvent was removed under vacuum. The product was precipitated from dichloromethane with ether. The complex [($CpCO_2CH_2C{\equiv}CH$)(η^6-C_6Me_6)Fe][PF_6], **37**, was obtained as an orange powder (2.35 g, 80% yield). ^{1}H NMR (CH_3COCH_3, 250 MHz), δ_{ppm}: 5.23 and 5.07 (s, 4H, Cp), 5.07 (s, 2H, OCH_2), 3.31 (s, 1H, C≡C*H*), 2.54 (s, 18H, C_6Me_6). ^{13}C NMR (CH_3COCH_3, 62.50 MHz), δ_{ppm}: 165.9 (C=O), 100.8 (Cq of C_6Me_6), 90.9 (Cq of Cp), 82.2 and 79.1 (CH of Cp), 81.7 (*C*≡CH), 77.8 (C≡*C*H), 53.8 (OCH_2), 17.2 (CH_3 of C_6Me_6). Anal. Calcd for $C_{21}H_{25}O_2FePF_6$: C 49.41, H 4.90; found: C 49.57, H 4.94. IR $\nu_{c=o}$: 1726 cm^{-1}.

[CpFe(η^6-C_6Me_6)CONHCH$_2$C≡CH][PF_6], 38. A suspension of [CpFe(η^6-C_6Me_6)COOH][PF_6] (0.550 g, 1.17 mmol) was heated in refluxing $SOCl_2$ (40 mL) for 16 h, and an homogeneous red solution was obtained; $SOCl_2$ was then removed using a trap-to-trap system under nitrogen atmosphere, and the complex **3** was obtained as a red powder. This complex **3** was dissolved in dry dichloromethane and slowly added to a dichloromethane solution of propargylamine (0.129 g, 2.34 mmol) and triethylamine (2 mL). The mixture was stirred under nitrogen atmosphere for 2 h at room temperature. The solvent was removed under vacuum, and the solid residue was dissolved in dichloromethane and washed with an aqueous solution of K_2CO_3, then with an aqueous solution of HPF_6. The organic solution was dried over sodium sulfate, filtered and the solvent removed under vacuum, then the solid product was precipitated from a dichloromethane solution using ether. The complex **38** was obtained as an orange powder (0.470 g, 80% yield). ^{1}H NMR (CH_3COCH_3, 300 MHz), δ_{ppm}: 8.03 (s, 1H, N*H*), 5.11 and 4.89 (s, 5H, Cp), 4.18 (m, 2H, NHCH_2), 2.78 (s, 1H, C≡C*H*), 2.45 (s, 18H, C_6Me_6). ^{13}C NMR (CH_3COCH_3, 62.90 MHz), δ_{ppm}: 163.6 (*C*=O), 100.4 (C_q of C_6Me_6), 84.2 (C_q of Cp), 81.2 and 77.2 (*C*H of Cp), 80.5 (*C*≡CH), 72.7 (C≡*C*H), 48.1 (NH*C*H_2), 17.0 (*C*H_3 of C_6Me_6). Anal. Calcd for $C_{21}H_{26}$ON-FePF$_6$: C 49.53, H 5.15; found: C 48.38, H 5.02. IR $\nu_{C=O}$: 1667 cm^{-1}.

General Procedure for the Synthesis by "Click" Reactions of the Dendrimers G_n-*n*-[Fe(η^5-$C_5H_4COXCH_2$-1,2,3-triazolyl-dendr)(η^6-C_6Me_6)] [PF_6], (*n* = 1, 2, 4, 7 ; X = O/NH). The complexes **37** or **38** (1.5 equiv per branch) dissolved in 30 mL of degassed dichloromethane was added to a solution of the azido dendrimer in 30 mL of degassed dichloromethane, and 60 mL of degassed water (1:1 dichloromethane/water) was added. A solution of $CuSO_4$ 1 M (1 equiv per branch) was added at 0 °C, followed by the dropwise addition of a freshly prepared solution of sodium ascorbate 1 M (2 equiv per branch). The reaction mixture was allowed to stir for 24 h under nitrogen atmosphere at room temperature. An aqueous solution of ammonia was then added, and the mixture was allowed to stir 10 min to remove all the copper trapped inside the dendrimer. The organic phase was washed twice with water, dried over sodium sulfate, filtered, and the solvent was removed under vacuum. The product was then washed with methanol to remove the excess alkyne and precipitated from an acetonitrile solution with methanol.

G_0-9-[Fe(η^5-$C_5H_4CO_2CH_2$-1,2,3-triazolyl-dendr)(η^6-C_6Me_6)][PF_6], 39. The complex **39** was synthesized from **37** (0.242 g, 0.486 mmol) and G_0-9-long-N_3 **33** (0.1 g, 0.036 mmol) using the general procedure for the synthesis by "click" reactions of the dendrimers G_n-*n*-[Fe(η^5-$C_5H_4COXCH_2$-1,2,3-triazolyl-dendr)(η^6-C_6Me_6)][PF_6], (n = 1, 2, 4, 7 ; X = O/NH). The complex **39** was obtained as an orange powder (0.232 g, yield 89%). ^{1}H NMR (CH_3COCH_3, 250 MHz), δ_{ppm}: 8.23 (s, 9H, CH of triazole), 7.10 (s, 3H, CH core), 5.48 (s, 18H, OCH_2-triazole), 5.16 and 5.02 (s, 36H, Cp), 4.45 (t, 18H, triazole-CH_2CH_2), 2.47 (s, 162H, C_6Me_6), 1.94 (m, 18H, triazole-CH_2CH_2), 1.72 (m, 36H, $CH_2CH_2CH_2Si$), 1.30 (m, 162H, $(CH_2)_9$), 1.21 (t, 36H, $CH_2CH_2CH_2Si$), 0.51 (s, 36H, CH_2SiCH_2), −0.03 (s, 54H, Si(CH3)2). ^{13}C NMR (CH_3COCH_3, 62.5 MHz), δ_{ppm}: 166.3 (C=O), 146.6 (Cq of triazole), 142.5 (Cq of arom. core), 132.2 (CH of triazole), 125.9 (CH of arom. core), 100.7 (Cq of C_6Me_6), 90.9 (Cq of Cp), 82.0 and 79.1 (CH of Cp), 69.7 (OCH_2-triazole), 59.6 (triazole-CH_2CH_2), 55.4 (triazole-CH_2CH_2), 50.8 (triazole-CH_2CH_2 CH_2), 44.7 ($C_qCH_2CH_2CH_2Si$), 43.0 (benzylic C_q), 34.7 (triazole-CH_2CH_2 CH_2 CH_2), 32.08 (triazole-CH_2CH_2 CH_2 CH_2CH_2), 27.3 and 24.8 ($(CH_2)_4CH_2CH_2Si$), 23.8 (CH_2CH_2Si), 18.9 ($C_qCH_2CH_2CH_2Si$), 18.8 ($(CH_2)_4CH_2CH_2Si$), 17.1 (CH_3 of C_6Me_6), 16.9 ($C_qCH_2CH_2CH_2Si$), 16.2 ($(CH_2)_4CH_2CH_2Si$), −2.5 ($Si(CH_3)_2$). Anal. Calcd for $C_{342}H_{534}O_{18}N_{27}Si_9Fe_9P_9F_{54}$: C 55.73, H 7.25; found: C 55.12, H 7.21. IR $\nu_{c=o}$: 1721 cm^{-1}.

G_1-27-[Fe(η^5-$C_5H_4CO_2CH_2$-1,2,3-triazolyl-dendr-)(η^6-C_6Me_6)]-[PF_6], 40. The metallodendrimer **40** was synthesized from the azido dendrimer G_1-long-N_3 **34** (0.1 g, 0.01 mmol) and **37** (0.200 g, 0.402 mmol) using the general procedure for the synthesis by "click" reactions of the dendrimers G_n-*n*-[Fe(η^5-$C_5H_4COXCH_2$-1,2,3-triazolyl-dendr)(η^6-C_6Me_6)] [PF_6], (n = 1, 2, 4, 7 ; X = O/NH). The complex **31** was obtained as an orange powder (0.215 g, 92% yield). ^{1}H NMR (CD_3CN, 200 MHz), δ_{ppm}: 7.99 (s, CH of triazole), 7.21 (d, arom.), 6.85 (d, arom.), 5.45 (s, OCH_2-triazole), 4.97 and 4.79 (s, Cp), 4.41 (t, triazole-CH_2CH_2), 3.54 (s, $SiCH_2O$), 2.39 (s, C_6Me_6), 1.91 (t, triazole-CH_2CH_2), 1.66 (s, $CH_2CH_2CH_2Si$), 1.29 (m, $(CH_2)_9$), 1.15 (t, $CH_2CH_2CH_2Si$), 0.47 (t, CH_2SiCH_2), −0.06 (s, 216H, Si(CH3)2). ^{13}C NMR (CD_3CN, 50 MHz), δ_{ppm}: 165.5 (C=O), 146.0 (Cq of triazole), 137.1 (arom. C_q), 131.8 (CH of triazole), 99.9 (Cq of C_6Me_6), 90.9 (Cq of Cp), 80.7 and 78.9 (CH of Cp), 69.7 (OCH_2-triazole), 58.9 (triazole-CH_2CH_2), 42.3 ($C_qCH_2CH_2CH_2Si$), 36.9 (triazole-CH_2CH_2 CH_2 CH_2), 33.7 (triazole-CH_2CH_2 CH_2 CH_2CH_2), 29.5 ($(CH_2)_4CH_2CH_2Si$), 26.4 (CH_2CH_2Si), 23.8 ($C_qCH_2CH_2CH_2Si$), 19.4 ($(CH_2)_4CH_2CH_2Si$), 18.00 (CH_3 of C_6Me_6), 16.2 ($C_qCH_2CH_2CH_2Si$), 15.4 ($(CH_2)_4CH_2CH_2Si$), −3.3 ($Si(CH_3)_2$). Anal. Calcd for $C_{1125}H_{1458}O_{63}N_{81}Si_{36}Fe_{27}P_{27}F_{162}$: C 57.36, H 6.19, found: C 56.39; H 0.5.96 IR $\nu_{c=o}$: 1721 cm^{-1}.

G_0-9-[Fe(η^5-$C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-)(η^6-C_6Me_6)]-[PF_6], 41. The dendrimer **41** was synthesized from G_0-long-N_3 **33** (0.060 g, 0.0216 mmol) and **38** (0.145 g, 0.292 mmol) using the general procedure for the synthesis by "click" reactions of the dendrimers G_n-*n*-[Fe(η^5-$C_5H_4COXCH_2$-1,2,3-triazolyl-dendr)(η^6-C_6Me_6)] [PF_6], (n = 1, 2, 4, 7 ; X = O/NH). The complex **41** was obtained as an orange powder (0.136 g, 87% yield). ^{1}H NMR (CH_3COCH_3, 300 MHz), δ_{ppm}: 8.21 (s, 9H, N*H*), 7.95 (s, 9H, C*H* of triazole), 7.09 (s, 3H, C*H* core), 5.16 and 4.90 (s, 45H, Cp), 4.62 (s, 18H, $NHCH_2$-triazole), 4.40 (t, 18H, triazole-CH_2CH_2), 2.43 (s, 162H, C_6Me_6), 1.87 (t, 18H, triazole-CH_2CH_2), 1.58 (s, 36H, $CH_2CH_2CH_2Si$), 1.32 (m, 180H, $(CH_2)_9$ and $CH_2CH_2CH_2Si$), 0.51 (s, 36H, CH_2SiCH_2), −0.36 (s, 54H, $Si(CH_3)_2$). ^{13}C NMR (CH_3COCH_3, 75.0 MHz), δ_{ppm}: 162.8 (*C*=O), 145.7 (C_q of arom. core), 143.2 (C_q of triazole), 123.0 (*C*H of triazole), 121.3 (*C*H of arom. core), 99.4 (C_q of C_6Me_6), 83.7 and 78.3 (C_q of Cp), 80.2 and 76.3 (*C*H of Cp), 71.7 (triazole-CH_2CH_2), 49.8 ($NHCH_2$-triazole), 43.7 ($C_qCH_2CH_2CH_2Si$), 42.0 (benzylic C_q), 34.9 (triazole-CH_2CH_2), 29.2 ($(CH_2)_7$), 23.8 (CH_2CH_2Si), 17.9 ($C_qCH_2CH_2CH_2Si$), 16.0 (CH_3 of C_6Me_6), 14.9 ($C_qCH_2CH_2CH_2Si$), −3.6 ($Si(CH_3)_2$). ^{29}Si NMR (CH_3COCH_3, 59.62 MHz), δ_{ppm}: 2.13 (*Si*Me_2). MS (MALDI-TOF; *m*/*z*), calcd. for $C_{342}H_{543}Si_9O_9N_{36}Fe_9P_8F_{48}$ (M^+): 7 218.38, found: 7 215.06. Anal. Calcd for $C_{342}H_{543}Si_9O_9N_{36}Fe_9P_9F_{54}$: C 55.79, H 7.43; found: C 54.93, H 7.34.

G_1-27-[Fe(η^5-$C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-)(η^6-C_6Me_6)][PF_6], 42. The dendrimer **42** was synthesized from G_1-long-N_3 **34** (0.050 g, 0.00496 mmol) and **38** (0.099 g, 0.198 mmol) using the general procedure for the synthesis by "click" reactions of the dendrimers G_n-*n*-[Fe(η^5-$C_5H_4COXCH_2$-1,2,3-triazolyl-dendr)-(η^6-C_6Me_6)][PF_6], (n = 1, 2, 4, 7 ; X = O/NH), giving **42** as an orange powder (0.089 g, 76% yield). ^{1}H NMR (CH_3COCH_3, 300 MHz), δ_{ppm}: 8.21 (s, 27H, N*H*), 7.99 (s, 27H, C*H* of triazole), 7.24 (d, 54H, arom), 6.89 (d, 54H, arom), 5.21 and 4.95 (s, 45H, Cp), 4.66 (s, 54H, $NHCH_2$-triazole), 4.24 (t, 54H, triazole-CH_2CH_2), 3.58 (s, 18H, CH_2O), 2.48 (s, 486H, C_6Me_6), 1.92 (t, 54H, triazole-CH_2CH_2), 1.70 (s, 72H, $CH_2CH_2CH_2Si$), 1.31 (m, 144H, $(CH_2)_9$), 0.52 (s, 126H, CH_2SiCH_2), −0.050 (s, 54H, $Si(CH_3)_2$). ^{13}C NMR (CH_3COCH_3, 75.0 MHz), δ_{ppm}: 162.7 (*C*=O), 158.9 (arom. OC_q), 144.0 (C_q of triazole), 139.1 (arom. C_q), 126.9 and 113.5 (arom. *C*H of dendron), 122.9 (*C*H of triazole), 99.6 (C_q of C_6Me_6), 83.7 and 78.3 (C_q of Cp), 80.2 and 76.3 (*C*H of Cp), 71.7 (triazole-CH_2CH_2), 59.8 ($SiCH_2O$), 49.6 ($NHCH_2$-triazole), 42.6 (C_q-$CH_2CH_2CH_2Si$), 41.2 (benzylic C_q), 34.7 (triazole-CH_2CH_2), 29.2 ($(CH_2)_7$), 23.8 (CH_2CH_2Si), 17.9 ($C_qCH_2CH_2CH_2Si$), 16.0 (CH_3 of C_6Me_6), 14.9 ($C_qCH_2CH_2CH_2Si$), −3.7 ($Si(CH_3)_2$). ^{29}Si NMR (CH_3COCH_3, 59.62 MHz), δ_{ppm}: 2.13 (*Si*$(Me)_2$). Anal. Calcd for $C_{1125}H_{1485}Si_{36}O_{36}N_{108}Fe_{27}P_{27}F_{162}$: C 57.42, H 6.36; found: C 57.04, H 6.23.

G_4-729-[Fe(η^5-$C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-)(η^6-C_6Me_6)][PF_6], 43. The dendrimer **43** was synthesized from G_4-long-N_3, **35**, (0.045 g, 1.52. 10^{-4} mmol) and **38** (0.083 g, 0.166 mmol) with the general procedure for the synthesis by "click" reactions of the dendrimers G_n-*n*-[Fe(η^5-$C_5H_4COXCH_2$-1,2,3-triazolyl-dendr)(η^6-C_6Me_6)] [PF_6], (n = 1, 2, 4, 7 ; X = O/NH), giving **43** as an orange powder (0.061 g, 61% yield). ^{1}H NMR (CH_3COCH_3, 300 MHz), δ_{ppm}: 8.25 (s, N*H*), 7.98 (s, C*H* of triazole), 7.21 (d, arom), 6.88 (d, arom), 5.20 and 4.93 (s, Cp), 4.64 (s, $NHCH_2$-triazole), 4.42 (t, triazole-CH_2CH_2), 3.56 (s, CH_2O), 2.46 (s, zC_6Me_6), 1.91 (t, triazole-CH_2CH_2), 1.68 (s, $CH_2CH_2CH_2Si$), 1.29 (m, $(CH_2)_9$), 0.48 (s, CH_2SiCH_2), −0.067 (s, $Si(CH_3)_2$). ^{13}C NMR (CH_3COCH_3, 75.0 MHz), δ_{ppm}: 162.7 (*C*=O), 158.8 (arom. OC_q), 144.1 (C_q of triazole), 139.1 (arom. C_q), 126.7 and 113.5 (arom. *C*H of dendron), 122.9 (*C*H of triazole), 99.4 (C_q of C_6Me_6), 83.7 and 78.3 (C_q of Cp), 80.2 and 76.3 (*C*H of Cp), 71.7 (triazole-CH_2CH_2), 59.8 ($SiCH_2O$), 49.6 ($NHCH_2$-triazole), 42.6 ($C_qCH_2CH_2CH_2Si$), 41.2 (benzylic C_q), 34.8 (triazole-CH_2CH_2), 29.1 ($(CH_2)_7$), 23.8 (CH_2CH_2Si), 17.9 ($C_qCH_2CH_2CH_2Si$), 16.0 (CH_3 of C_6Me_6), 14.9 ($C_qCH_2CH_2CH_2Si$), −3.7 ($Si(CH_3)_2$). ^{29}Si NMR (CH_3COCH_3, 59.62 MHz), δ_{ppm}: 2.13 (*Si*$(Me)_2$). Anal. Calcd for $C_{31662}H_{50223}O_{1089}Si_{1089}N_{2916}Fe_{729}P_{729}F_{4374}$: C 57.09, H 12.47; found: C 55.01, H 12.23.

G_7-19683-[Fe(η^5-$C_5H_4CONHCH_2$-1,2,3-triazolyl-dendr-)(η^6-C_6Me_6)][PF_6], 44. The dendrimer **44** was synthesized from G_7-long-N_3, **36**, (0.040 g, 5 × 10^{-6} mmol) and **38** (0.073 g, 0.148 mmol) with the general procedure for the synthesis by "click" reactions of the dendrimers G_n-*n*-[Fe(η^5-$C_5H_4COXCH_2$-1,2,3-triazolyl-dendr)(η^6-C_6Me_6)][PF_6], (n = 1, 2, 4, 7 ; X = O/NH), giving **44** as an orange powder (0.046 g, 52% yield). ^{1}H NMR (CH_3COCH_3, 300 MHz), δ_{ppm}: 8.17 (s, N*H*), 7.95 (s, C*H* of triazole), 7.21 (d, arom), 6.88 (d, arom), 5.20 and 4.93 (s, Cp), 4.64 (s, NHCH_2-triazole), 4.41 (t, triazole-CH_2CH$_2$), 3.56 (s, CH_2O), 2.46 (s, C_6Me_6), 1.91 (t, triazole-CH$_2$CH_2), 1.71 (s, CH_2CH$_2$CH$_2$Si), 1.29 (m, (CH_2)$_9$), 0.51 (s, CH_2SiCH_2), −0.064 (s, Si(CH_3)$_2$). ^{13}C NMR (CH_3COCH_3, 75.0 MHz), δ_{ppm}: 162.7 (*C*=O), 158.7 (arom. OC_q), 144.2 (C_q of triazole), 139.1 (arom. C_q), 126.7 and 113.5 (arom. *C*H of dendron), 122.7 (*C*H of triazole), 99.3 (C_q of C_6Me_6), 83.7 and 78.3 (C_q of Cp), 80.2 and 76.3 (*C*H of Cp), 71.7 (triazole-*C*H$_2$CH$_2$), 59.8 (Si*C*H$_2$O), 49.6 (NH*C*H$_2$-triazole), 42.5 (C_q*C*H$_2$CH$_2$CH$_2$Si), 41.2 (benzylic C_q), 34.8 (triazole-CH$_2$*C*H$_2$), 29.1 ((CH$_2$)$_7$), 23.8 (*C*H$_2$CH$_2$Si), 17.9 (C_qCH$_2$*C*H$_2$CH$_2$Si), 16.2 (*C*H$_3$ of C_6Me_6), 14.9 (C_qCH$_2$-CH$_2$*C*H$_2$Si), −3.7 (Si(*C*H$_3$)$_2$). ^{29}Si NMR (CH_3COCH_3, 59.62 MHz), δ_{ppm}: 2.13 (*Si*(Me)$_2$). Anal. Calcd for $C_{856161}H_{1358049}O_{29520}Si_{29520}N_{78732}Fe_{19683}P_{19683}F_{118098}$: C 57.10, H 7.60; found: C 53.61, H 7.32.

[Fe(η^5-$C_5H_4CO_2^-Na^+$)(η^6-C_6Me_6)][PF_6], 2a. The complex **2** (0.150 g, 0.3178) was added at ambient temperature to a solution of NaOH (0.013 g, 0.3178 mmol) in 5 mL of EtOH. After stirring for 5 min, the solvent was removed under vacuum, giving **2a** as an orange powder (0.160 g; 98% yield). ^{1}H NMR (CD_3CN, 200 MHz), δ_{ppm}: 4.73 and 4.45 (s, 4H, Cp), 2.37 (s, 18H, C_6Me_6). ^{13}C NMR (CD_3CN, 50 MHz) δ_{ppm}: 168.6 (C=O), 98.5 (C_6Me$_6$), 89.3 (Cq of Cp), 79.1 and 78.4 (CH of Cp), 16.0 (CH$_3$ of C_6Me_6).

Reaction between C_{60} and 22a with Formation of G$_4$-DAB-64-[Fe^{II}(η^5-C_5H_4CONH-dendr)(η^6-C_6Me_6)][$C_{60}^{\bullet -}$], 45. **1** (0.040 g, 0.099 mmol), in 10 mL of THF was stirred with 4.6 g of Na/Hg amalgam (1%, 2 mmol) for 1 h under N_2. Then, THF was removed under vacuum, the residue of **1** was extracted with 15 mL of pentane, and this forest-green solution of **1** was used for the following reaction. This solution was slowly added to a CH_3CN solution (15 mL) of **22** (0.050 g, 0.0014 mmol) upon stirring at −40 °C until the solution turned from forest-green to blue-green (equivalence point of the titration), indicating the formation of **22a**. The solution of **22a** at −40 °C was slowly added to a 30-mL toluene solution of C_{60} (0.063 g, 0.088 mmol) at −40 °C, which immediately provoked the formation of a precipitate, until the blue-green color persisted in solution (equivalence point of the titration). The solvent was removed under vacuum, and the residue was washed twice with CH_3CN (the yellow extracts contained **1** as verified by ^{1}H NMR), and with toluene (colorless extract). The black powder of **45** was dried under vacuum and was kept under N_2 (0.091 g, 0.00127 mmol, 91% yield). The organic solvent resulting from the washing was removed under vacuum and 0.032 g (0.079 mmol, 80%) of **1** was recovered. EPR spectrum of **45** at 298 K (see Figure 3): g = 2.00093; ΔH = 3.12 G. Mössbauer spectrum of **45** at 77 K: a simple quadrupole doublet (QS = 1.97 mm/s; IS = 0.56 mm/s vs Fe), characteristic of the salts of **1**.[4a,12a]

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Supporting Information Available: General data and ^{1}H and ^{13}C NMR and IR spectra of new products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.