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Visible-Light Photolytic Synthesis of Multinuclear and Dendritic Iron-Nitrile Cationic Complexes

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Multinuclear and dendritic iron-nitrile piano-stool cationic complexes were synthesized in quantitative yield by a single-step synthesis involving visible-light photolysis of the complex [CpFe(η^6-toluene)][PF$_6$]. This synthetic strategy was applied to mono-, bis- and tris-nitrile ligands and to new nitrile-terminated dendrimers containing 9, 27, and 81 tethers. All the synthesized products are deep red solids or red waxy products, highly stable to air and moisture. They were characterized by ^{1}H, ^{13}C, and ^{31}P NMR, elemental analysis, UV–vis spectroscopy, and cyclic voltammetry (single reversible oxidation wave to Fe^{III}). Only the *para*-disubstituted arene dinitrile diiron complex shows two separated reversible waves indicating some electronic communication between the iron centers through the nitrile ligands.

Introduction

In the promising field of molecular electronics,[1] polynuclear compounds featuring redox-active organometallic end groups seem especially attractive from various perspectives, in particular for information storage and processing.[2] In the past decade, the study of transition metal-acetylides complexes has showed that M−C≡C fragments are particularly interesting building blocks for the construction of molecular devices.[3]

Nitrile ligands are isoelectronic with acetylide, and the interest in them has recently resurfaced because of the observations of significant second order nonlinear optical responses.[4,5] The synthesis of piano-stool iron-nitrile complexes usually involves several steps including tedious purification processes.[4,5]

The robust, air stable 18-electron complexes [CpFe(η^6-arene)][PF$_6$] are a very broad family,[6,7] and their photolysis have been applied in organic synthesis,[8] electron-transfer processes,[9] molecular electronics,[10] and dendrimer chemistry.[11] Our interest is in their application to the synthesis of piano-stool iron-nitrile complexes. The visible-light photo-

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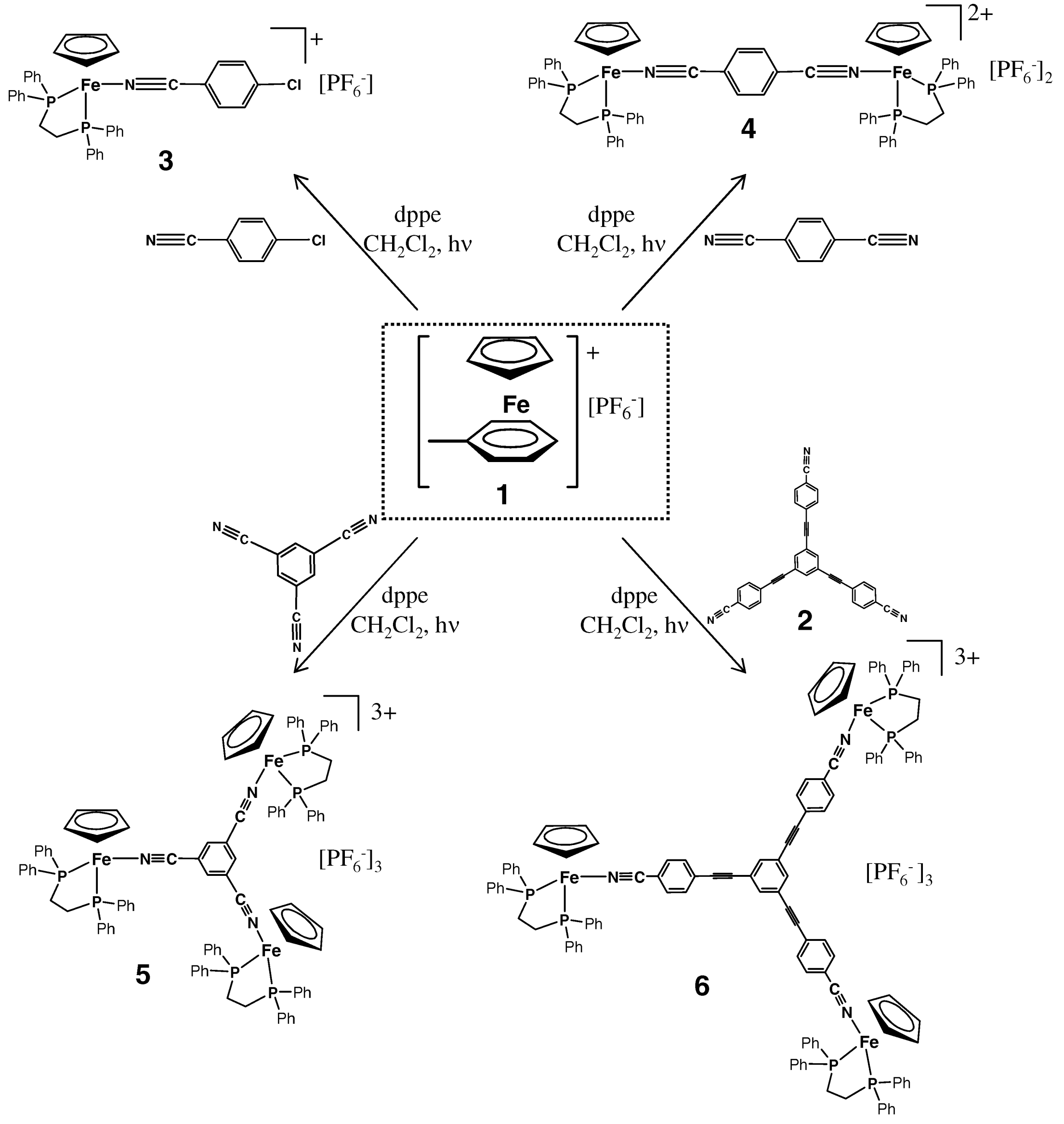
Scheme 1. Photochemical Synthesis of Mono-, Bis- And Tri-nuclear Iron-Nitrile Piano-Stool Complexes



chemical reaction yielding piano-stool complexes was reported in 1983 by Mann's group[12] and our group.[13] Mann's report involved the synthesis of the piano-stool organo-iron complex $[CpFe(MeCN)_3][PF_6]$, containing three acetonitrile ligands, upon photolysis of $[CpFe(\eta^6\text{-arene})][PF_6]$ complexes using acetonitrile as solvent; this compound was found to be unstable above −30 °C. Similar reactions, carried out in the presence of a diphosphine (diphos) directly leads to the piano-stool complexes of the type $[CpFe(dppe)NCMe][PF_6]$.[14] Nevertheless, all the reported reactions for the photolysis of $[CpFe(\eta^6\text{-arene})][PF_6]$ complexes were carried out using high excess of MeCN ligand (used as solvent).

We now report that this reaction can be extended to polynitrile ligands other than acetonitrile, including conjugated polynitrile ligands and hyperbranched dendrimers. This synthetic approach allows a one-step synthesis of multinuclear organo-iron piano-stool complexes and dendrimers, in quantitative yield, using only a stoichiometric amount of nitrile ligand.

Results and Discussion

1. One-Step Synthesis of Iron-Nitrile Complexes and Dendrimers by Photolysis of Complex 1. The photolysis of the complex $[CpFe(\eta^6\text{-toluene})][PF_6]$, **1**, is shown here to be a clean synthetic strategy to easily obtain multinuclear

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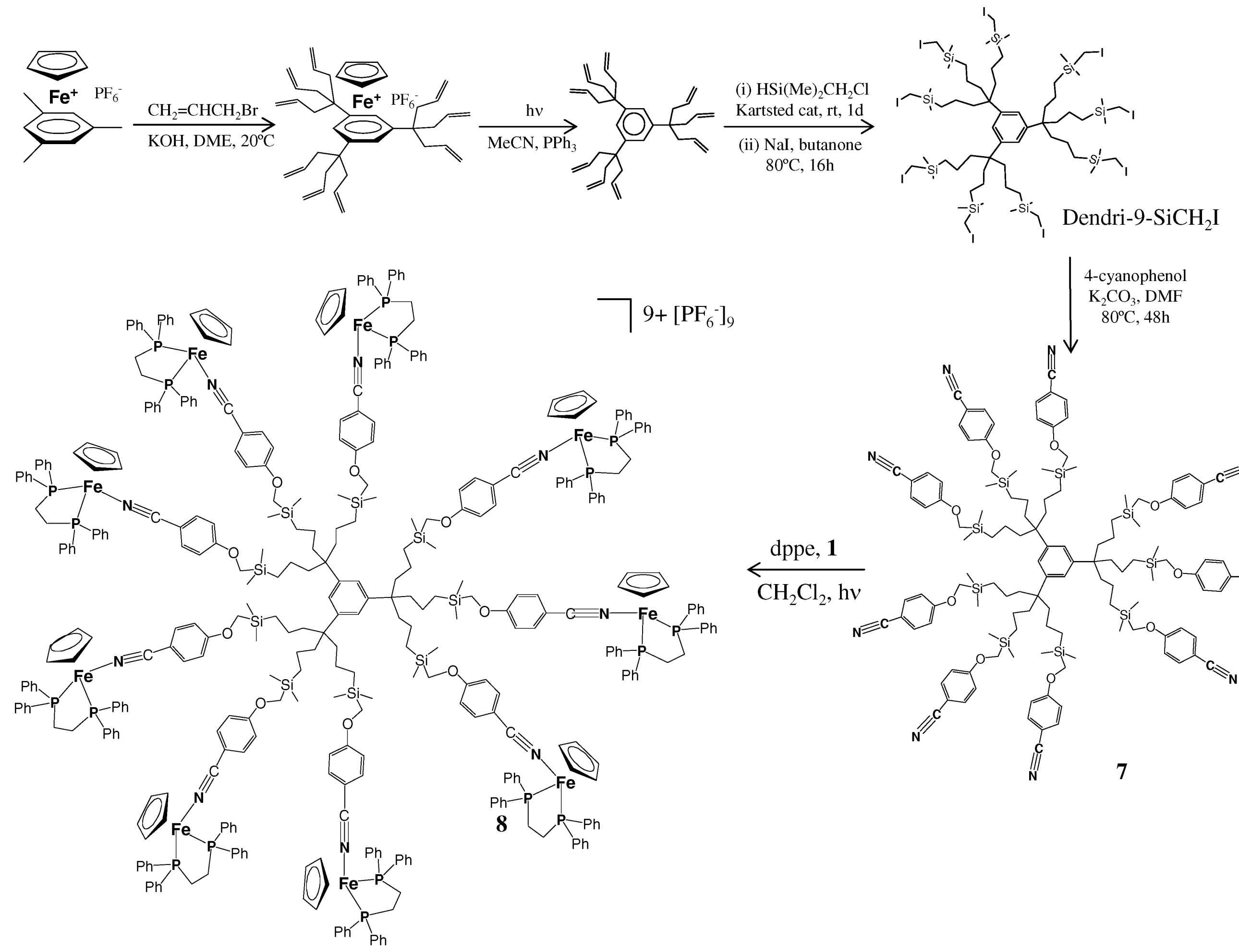
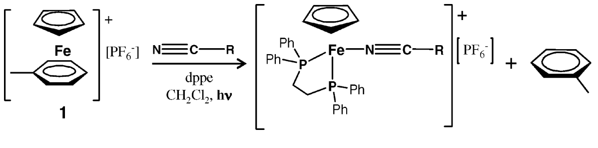
Scheme 2. Synthesis of the Nona-Iron Dendrimer **8** by Photochemistry



iron-nitrile complexes. The reactions are carried out in dichloromethane (weakly coordinating solvent), using stoichiometric amounts of [CpFe(η^6-toluene)][PF_6], bis(diphenylphosphino)ethane (dppe), and nitrile ligand, and the reaction mixture is exposed to visible light overnight. The reaction quantitatively yields the iron-nitrile complexes [CpFe(dppe)(RCN)][PF_6], and the only side-product is toluene which can be easily removed under vacuum (eq 1). No reaction occurs in the dark.



(1)

The first attempt to accomplish this reaction was made using the mononitrile ligand 1,4-chlorobenzonitrile, quantitatively yielding the corresponding iron-nitrile complex **3** (Scheme 1).

The reaction mixture was irradiated with visible light for one night, and the solution color changed from light green (**1**) to deep red (**3**). After removing the solvent under vacuum, the crude product was analyzed without further purification. The ^{31}P NMR spectrum, besides the septuplet of the PF_6 anion, clearly shows only one peak at 97 ppm that corresponds to the phosphorus of *P*-Fe atoms of the complex [CpFe(dppe)(RCN)][PF_6]. This confirms that the stoichiometric amount of dppe added was all consumed to form the expected complex. The ^{1}H NMR spectra is also in agreement with the expected complex showing only one peak for the Cp protons at 4.67 ppm. The IR spectrum of the crude product shows only one nitrile band at 2214 cm^{-1} different from those of the free ligand.

Once the reaction was successfully accomplished with the mononitrile ligand, we extended this synthetic approach to polynitrile ligands including bis-[15] and tris-nitrile ligands. This synthesis afforded in one-step highly stable electron-rich multinuclear complexes in quantitative yield (Scheme 1).

Dendrimers containing robust redox termini have interesting applications in redox sensing and molecular electronics.[16] Dendrimers containing organometallics sandwich complexes at the periphery, such as ferrocene, have been widely studied,[16] but dendrimers possessing robust piano-stool complexes are not known besides our work.[17]

The one-step synthesis of iron-nitrile complexes reported here was extended to dendrimer chemistry by synthesizing

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nitrile-terminated dendrimers and using them as nitrile ligands in the photolysis of complex **1**.

The nonanitrile dendrimer **7** was obtained in high yield by the Williamson reaction between the known nonaiodomethylsilyl dendrimer[11b] and 4-cyanophenol in dimethylformamide (DMF), 80 °C for 48 h, and purified by precipitation with methanol. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrum of dendrimer **7** shows its molecular peak at 2223.11 (MNa, calcd for $C_{126}H_{165}N_9NaO_9Si_9$: 2223.05). The nonanitrile dendrimer **7** was used as nitrile ligand in the photolysis of complex **1**, and the corresponding nona-iron complex **8** was obtained as a deep red waxy product, in quantitative yield (Scheme 2).

We have extended this reaction to dendrimers of higher generations (27 and 81 branches). For this purpose, we have first lengthened the dendrimer tethers to avoid bulk between the termini during the photochemical reaction.

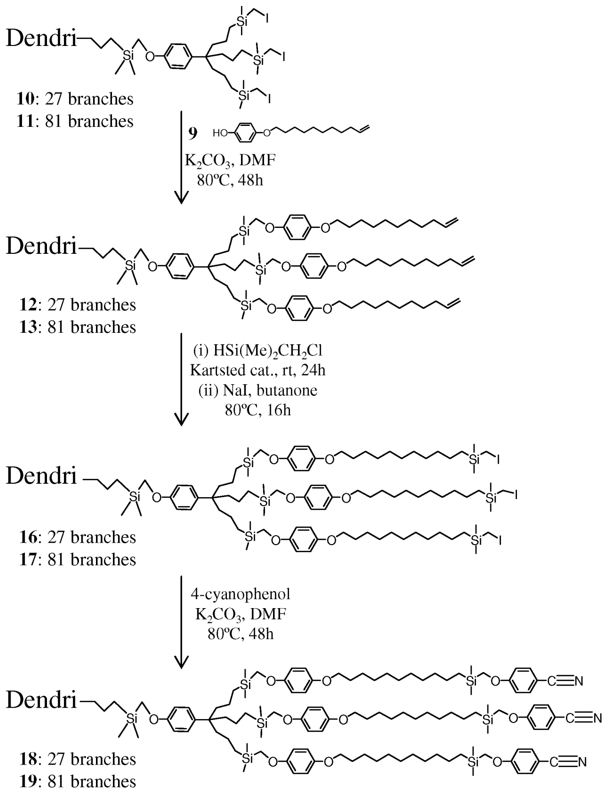
Lengthening of the dendrimers tethers was performed by the Williamson reaction between the 27- and 81-iodomethylsilyl dendrimers (**10** and **11** respectively)[11b] with *p*-hydroxyphenyl undecene-1-yl ether (**9**), giving the polyallyl dendrimers with long tethers **12** (27-long-allyl) and **13** (81-long-allyl). The dendrimers **12** and **13** were further submitted to hydrosilylation with (dimethyl)chloromethylsilane using Kartsted catalyst giving **14** (27-long-chloride) and **15** (81-long-chloride) followed by replacement of the chloride by the iodide giving **16** (27-long-iodide) and **17** (81-long-iodide). Finally, the Williamson reaction of **16** and **17** with 4-cyanophenol yielded the cyano-dendrimers **18** and **19** that contain 27- and 81-nitrile termini, respectively, and long tethers (Scheme 3).

Dendrimers **18** and **19** were used as nitrile ligands in the photolysis of complex **1**, and the corresponding multinuclear iron-nitrile dendrimers **20** and **21** were obtained as red waxy products in quantitative yields (Chart 1).

All the iron-nitrile terminated dendrimers present only one peak in the ^{31}P NMR spectra at 97 ppm, only one nitrile band at the IR spectra at 2 221 cm^{-1} and satisfactory elemental analysis, confirming that the one-step synthesis applied here is an efficient synthetic approach.

2. Characterization of the Iron-Nitrile Piano-Stool Complexes and Dendrimers by UV-vis Spectroscopy. All the iron-nitrile complexes and dendrimers reported here are red solids or red waxy products and present high stability to air and moisture. All the iron-nitrile complexes present two absorption bands in the visible region. In the mononuclear complex **3** these two bands appear at 341 and 387 nm. The first band corresponds to the Cp-Fe and the second one to the Fe to CN metal-to-ligand charge-transfer (MLCT) transitions. This latter attribution is consistent with the large variation of the ε values by metal center (compare **6**). The visible spectra of the dinuclear complex **4** and trinuclear complex **5** are quite different from that of the monoiron complex because of the electronic interaction between the close iron centers connected by the aromatic ring. In these complexes, the two visible bands appear at 408 and 469 nm for complex **4** and at 407 and 466 nm for complex **5**. The visible spectrum of the trinuclear complex **6** (373 and 421 nm) still presents a slight effect of the electronic interaction, although this effect is less significant than in complex **5**, probably because of the higher distance between the iron centers (it is known[3] that the electronic interaction is weaker in systems with higher distance between the metal centers, Figure 1). This difference in the electronic behavior between complex **5** and **6** is also observed by solid state Fourier transform infrared spectroscopy (FTIR, Table 1). A lowering on the position of the ν_{CN} frequency in complex **5** and **6** is observed, when compared with the free ligands, of -48 cm^{-1} and -10 cm^{-1}, respectively, showing that in the complex **6** the π back-donation from the metal d orbitals to the CN-π^* orbitals is probably less effective or even absent.

Scheme 3. Synthesis of 27- and 81-Nitrile Dendrimers with Long Tethers



The UV-vis spectra of the dendrimers also present two bands in the visible region, very similar to those of the monomer complex **3**, at 316 and 375 nm; the difference between the values found for the complex **3** and the dendrimers are caused by the donor character of the ether

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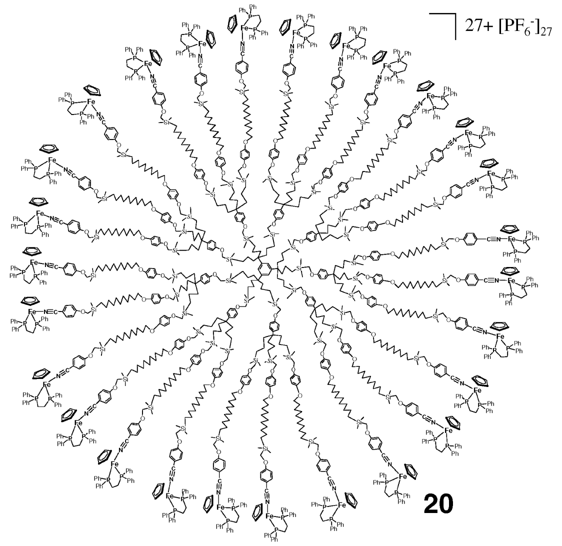
Chart 1. Dendrimers with 27 and 81 Piano-Stool Iron Complexes Synthesized by Light-Induced Reaction



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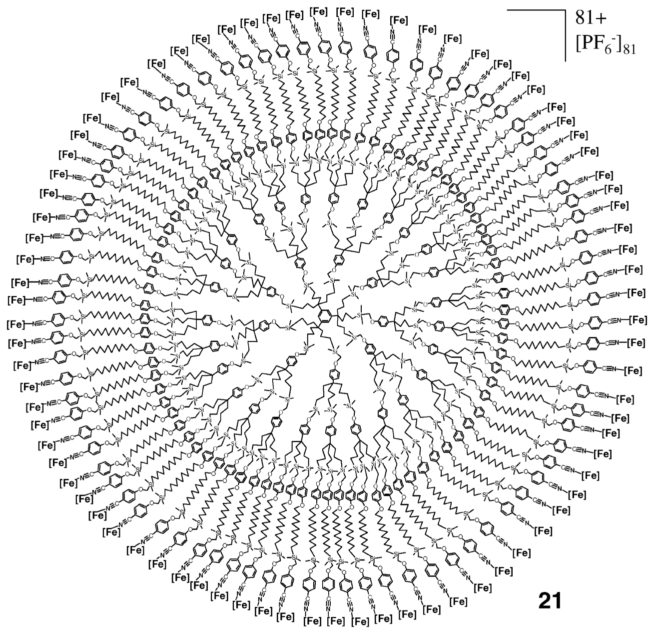

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[Fe]: CpFe(dppe)

group at the *para* position in the dendrimers compared with the acceptor character of the chlorine atom in the complex **3**.

3. Cyclic Voltammetry (CV) of the Iron-Nitrile Piano-Stool Complexes and Dendrimers. The iron-nitrile complexes and dendrimers were characterized by CV to study their redox properties. The complexes (except the binuclear complex **4**) and the dendrimers present only one redox wave that is completely reversible for the oxidation of Fe^{II} to Fe^{III} near 900 mV vs FeCp*$_2$ (Cp*= η^5-C$_5$Me$_5$; all the CV data are gathered in Table 1).

The PF$_6$ counteranion forms, with the complex, a contact ion-pair so that the electrostatic factor is minimized in all cases.[19] For the binuclear complex **4**, however, two redox waves are observed because of the electronic communication favored by the *para* position of the nitrile ligands in the benzene ring. The *meta* position of the iron-nitrile moieties in complex **5** disfavors the electronic communication,[20] which results in the observation of a single redox wave in the CV instead of three different redox waves that would be observed if the electronic communication was effective.

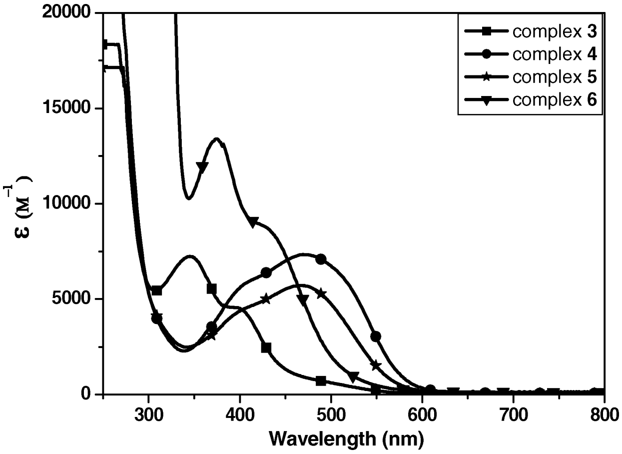

Figure 1. UV-vis spectra of complexes **3**−**6** (ε by metal center, i.e., divided by the number of metals in the complex).

Table 1. Electrochemical, IR, and ^{31}P NMR Data of the Complexes and Dendrimers

		IR		^{31}P NMR
product	CV[a] (mV)	υ_{CN} (cm^{-1})	υ_{PF6} (cm^{-1})	δ_{ppm} (Fe-*P*)
3	930	2214	840	97.04
4	1st, 925; 2nd, 1010	2208	838	96.84
5	980	2201	838	96.69
6	920	2215	837	96.98
8	845	2221	838	97.20
20	845	2221	838	97.37
21	845	2221	838	97.37

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$ vs FeCp$_2$* (in V). Electrolyte, [n-Bu$_4$N][PF$_6$] 0.1M; working and counter electrodes, Pt; reference electrode, Ag; internal reference, FeCp*$_2$;[18,19] scan rate, 0.200 V s^{-1}; 20 °C.

Conclusion

In this work, we have shown that photolysis of the complex [CpFe(η^6-toluene)][PF$_6$] is a clean one-step high-yielding synthetic strategy to easily obtain, in high yield, multinuclear iron-nitrile complexes and dendrimers up to 81 branches. These piano-stool iron complexes and dendrimers are robust and present high stability to air and moisture. These nitrile complexes show single fully reversible redox waves in CV except for the para-substituted dinitrilediiron complex. In the latter, the 85-mV separation between the two CV waves (no separation is observed in the 1,3,5-trisubstituted trinuclear complex) is the sign of some electronic communication between the two iron centers through the dinitrile ligand.

Experimental Section

General Data. The complex **1**,[2] ligand **2**,[21] the iodomethylsilyl-dendrimers **6**,[11b] **10**,[11b] and **11**,[11b] the allyl-dendrimers **12**[22] and

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13,[22] and the *p*-hydroxyphenyl undecene-1-yl ether (**9**)[22] were prepared according to our previous reports.

^{1}H NMR spectra were recorded at 25 °C with a Bruker AC 300 (300 MHz) spectrometer. ^{13}C NMR spectra were obtained in the pulsed FT mode at 75.0 MHz, ^{31}P NMR spectra were obtained at 59.6 MHz, and ^{29}Si NMR spectra were obtained at 59.6 MHz with a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS) as internal standard. CV: all electrochemical measurements were recorded under nitrogen atmosphere using a Princeton Applied Resarch 273 potentiostat-galvanostat. Solvent: dichloromethane; temperature, 20 °C; supporting electrolyte, $[nBu_4N][PF_6]$ 0.1M; working and counter electrodes, Pt; reference electrode, Ag; internal reference, $FeCp^*_2$;[18,19] scan rate, 0.200 V s^{-1}. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon Villeurbanne, France. The mass spectrum reported here is a MALDI TOF mass spectrum that was recorded with a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. The UV–vis spectra were recorded in dichloromethane at 25 °C on a Hewlett-Packard 8453 UV–vis spectrometer.

General Procedure for the Photochemical Reactions. In a double-wall Schlenk flask, stoichiometric amounts of complex **1**, dppe, and nitrile ligand were dissolved in dry dichloromethane. The solution was irradiated with visible light (ordinary lamp, 100 W) for 18 h, under magnetic stirring and water cooling on the exterior wall of the Schlenk tube (20 °C). The solvent was removed under vacuum, and the crude product was analyzed. Complexes **2**, **3**, **4**, and **5** were not submitted to further purification procedures and were obtained in quantitative yields. The metallodendrimers **8**, **20**, and **21** were precipitated with dichloromethane/methanol.

Synthesis of 3. The complex **3** was synthesized from **1** (0.500 g, 1.40 mmol), dppe (0.557 g, 1.40 mmol), and 4-chlorobenzonitrile (0.192 g, 1.40 mmol) following the general procedure for photochemical reactions.

^{1}H NMR (CD_3COCD_3, 300 MHz): 8.08–7.57 (m, 20H, arom. C*H* of dppe), 7.35 and 6.69 (d, 4H, arom. C*H*), 4.67 (s, 5H, Cp), 2.81 and 2.67 (m, 4H, CH_2CH_2 of dppe). ^{13}C NMR (CH_3COCH_3, 75.0 MHz): 139.7–130.0 (arom. of dppe and benzonitrile), 111.2 ($C{\equiv}N{-}Fe$), 80.9 (*C*H of Cp). ^{31}P NMR (CD_3COCD_3, 121 MHz): 97.04 (Fe^+-*P*), 126.6–161.6 (PF_6). Anal. Calcd for $C_{38}H_{33}NClF_6FeP_3$: C 56.92, H 4.15. Found: C 56.50, H 4.24. Infrared $\upsilon_{C\equiv N}$: 2 214 cm^{-1}, υ_{PF6}: 840.

Synthesis of 4. The complex **4** was synthesized from **1** (0.558 g, 1.56 mmol), dppe (0.622 g, 1.56 mmol), and 1,4-dicyanobenzene (0.100 g, 0.781 mmol) following the general procedure for photochemical reactions.

^{1}H NMR (CD_3COCD_3, 300 MHz): 8.02–7.18 (m, 40H, arom. C*H* of dppe), 6.52 (s, 4H, arom. C*H* of bridge), 4.67 (s, 10H, Cp), 2.81 and 2.66 (m, 8H, CH_2CH_2 of dppe). ^{13}C NMR (CH_3COCH_3, 75.0 MHz): 136.9–125.1 (arom. of dppe and benzonitrile), 114.5 ($C{\equiv}N{-}Fe$), 80.4 (*C*H of Cp). ^{31}P NMR (CD_3COCD_3, 121 MHz): 96.84 (Fe^+-*P*), 126.6–161.6 (PF_6). Anal. Calcd for $C_{70}H_{62}N_2F_{12}Fe_2P_6$: C 57.71, H 4.29. Found: C 57.87, H 4.55. Infrared $\upsilon_{C\equiv N}$: 2 208 cm^{-1}, υ_{PF6}: 838.

Synthesis of 5. The complex **5** was synthesized from **1** (0.708 g, 1.98 mmol), dppe (0.789 g, 1.98 mmol), and 1,3,5-tricyanobenzene (0.101 g, 0.660 mmol) following the general procedure for photochemical reactions.

^{1}H NMR (CD_3COCD_3, 300 MHz): 8.03–7.18 (m, 60H, arom. C*H* of dppe), 6.84 (s, 3H, arom. C*H* of bridge), 4.76, 4.73 and 4.71 (s, 15H, Cp), 2.81 and 2.66 (m, 12H, CH_2CH_2 of dppe). ^{13}C NMR (CH_3COCH_3, 75.0 MHz): 136.9–125.1 (arom. of dppe and benzonitrile), 113.5 ($C{\equiv}N{-}Fe$), 80.6 (*C*H of Cp). ^{31}P NMR (CH_3COCH_3, 121 MHz): 96.69 (Fe^+-*P*), 126.7–161.6 (PF_6). Anal. Calcd for $C_{102}H_{90}N_3F_{18}Fe_3P_9$: C 57.09, H 4.23. Found: C 57.04, H 4.43. Infrared $\upsilon_{C\equiv N}$: 2 201 cm^{-1}, υ_{PF6}: 838.

Synthesis of 6. The complex **6** was synthesized from **1** (0.147 g, 0.411 mmol), dppe (0.164 g, 0.411 mmol), and **2**[21] (0.062 g, 0.137 mmol) following the general procedure for photochemical reactions.

^{1}H NMR (CD_3COCD_3, 300 MHz): 8.03–7.57 (m, 60H, arom. C*H* of dppe), 7.42 and 6.70 (d, 12H, arom. C*H* of bridge), 4.68 (s, 15H, Cp), 2.81 and 2.68 (m, 12H, CH_2CH_2 of dppe). ^{13}C NMR (CH_3COCH_3, 75.0 MHz): 136.9–124.5 (arom. of dppe and benzonitrile), 112.4 (*C*N), 92.3 and 90.2 ($C{\equiv}C$), 81.0 (*C*H of Cp). ^{31}P NMR (CH_3COCH_3, 121 MHz): 96.98 (Fe^+-*P*), 126.7–161.6 (PF_6). Anal. Calcd for $C_{126}H_{102}N_3F_{18}Fe_3P_9$: C 61.86, H 4.20. Found: C 61.01, H 4.56. Infrared $\upsilon_{C\equiv N}$: 2 215 cm^{-1}, υ_{PF6}: 837.

Synthesis of 7. The 9-iodomethylsilyl dendrimer[11b] (0.320 g, 0.219 mmol), 4-cyanophenol (0.471 g, 3.95 mmol), and K_2CO_3 (2.76 g, 19.7 mmol) were introduced in a Schlenk flask, and dry DMF (20 mL) was added. The reaction mixture was stirred at 80 °C, for 48 h. The DMF was removed, 20 mL of CH_2Cl_2 were added, and the solution was filtered on celite to remove the K_2CO_3. The solvent was removed in vacuo, and the product was washed with methanol to remove the excess of starting material. The product was precipitated twice with dichloromethane/methanol, and **7** was obtained as a colorless waxy product in 89% yield (0.428 g).

^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 7.52 and 6.92 (d, 36H, arom.), 6.99 (s, 3H, arom. core), 3.53 (s, 18H, $SiCH_2O$), 1.62 (s, 18H, $CH_2CH_2CH_2Si$), 1.12 (s, 18H, $CH_2CH_2CH_2Si$), 0.57 (s, 18H, $CH_2CH_2CH_2Si$), 0.038 (s, 54H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 75.0 MHz), δ_{ppm}: 163.3 (C_qO), 144.6 (C_q, arom. core), 132.6 and 113.0 (*C*H, arom.), 120.2 ($C{\equiv}N$), 102.4 (C_q, arom.), 59.7 ($SiCH_2O$), 42.7 ($CH_2CH_2CH_2Si$), 16.5 ($CH_2CH_2CH_2Si$), 14.0 ($CH_2CH_2CH_2Si$), −5.9 ($SiMe_2$). ^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: 0.69 ($SiCH_2O$). MS (MALDI-TOF; *m/z*), calcd. for $C_{126}H_{165}N_9NaO_9Si_9$: 2 223.05. found 2 223.11. Anal. Calcd for $C_{126}H_{165}N_9O_9Si_9$: C 68.71, H 7.55. Found: C 68.61, H 7.28. Infrared: $\nu_{CN} = 2\ 224$ cm^{-1}.

Synthesis of 8. The metallodendrimer **8** was synthesized from **1** (0.157 g, 0.439 mmol), dppe (0.175 g, 0.439 mmol), and dendri-9-CN **7** (0.107 g, 0.0487 mmol) following the general procedure for photochemical reactions. The dendrimer **8** was obtained as a red waxy product in 98% yield (0.392 g).

^{1}H NMR (CD_3COCD_3, 300 MHz): 8.05, 7.53 and 7.09 (m, 60H, arom. C*H* of dppe), 6.84 and 6.59 (d, 36H, arom.), 4.59 (s, 45H, C*H* of Cp), 3.61 (s, 18H, $SiCH_2O$), 2.75 and 2.53 (m, 36H, CH_2CH_2 of dppe), 1.73 (s, 18H, $CH_2CH_2CH_2Si$), 1.22 (s, 18H, $CH_2CH_2CH_2Si$), 0.61 (s, 18H, $CH_2CH_2CH_2Si$), 0.026 (s, 54H, $Si(CH_3)_2$). ^{13}C NMR (CH_3COCH_3, 75.0 MHz): 164.5 (C_qO), 144.7 (C_q, arom. core), 136.9–124.5 (arom. of dppe and *C*H of benzonitrile), 115.1 (*C*H, arom.), 114.6 ($C{\equiv}N{-}Fe$), 102.8 (C_q, arom.), 79.5 (*C*H of Cp), 60.9 ($SiCH_2O$), 55.0 ($P(CH_2)_2P$) 43.9 ($CH_2CH_2CH_2Si$), 17.8 ($CH_2CH_2CH_2Si$), 14.1 ($CH_2CH_2CH_2Si$), −5.9 ($SiMe_2$). ^{31}P NMR (CD_3COCD_3, 121 MHz): 97.2 (Fe^+-*P*), 126.5–161.6 (PF_6). Anal. Calcd for $C_{405}H_{426}N_9F_{54}Fe_9O_9P_{27}Si_9$: C 59.46, H 5.25. Found: C 59.96, H 5.97. Infrared $\upsilon_{C\equiv N}$: 2 221 cm^{-1}, υ_{PF6}: 838.

Synthesis of 14. The polyolefin dendrimer **12**[22] (0.050 g, 0.0041 mmol), dry diethyl ether (30 mL), dimethylchloromethylsilane (0.024 g, 0.221 mmol), and Kartsted catalyst (0.1%) were succes-

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(21) Kiang, Y.-H.; Gardner, G. B.; Lee, S.; Xu, Z.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1999**, *121*, 8204–8215.

(22) Ornelas, C.; Méry, D.; Blais, J.-C.; Cloutet, E.; Aranzaes, J. R.; Astruc, D. *Angew. Chem., Int. Ed.* **2005**, *45*, 7399–7404.

sively introduced into a Schlenk flask under a nitrogen atmosphere. The reaction solution was stirred at 25 °C for 16 h. The solvent was removed under vacuum, the catalyst residue was removed by silica flash chromatography, and the dendrimer was precipitated using dichloromethane/methanol. The dendrimer **14** was obtained as a colorless waxy product in 92% yield (0.057 g).

^{1}H NMR (CDCl$_3$, 300 MHz): 7.22 (d, arom.), 7.09 (d, arom. core), 6.90 (d, arom.), 3.87 (t, OC*H*$_2$CH$_2$), 3.52 (s, inner SiC*H*$_2$O), 3.46 (s, outer SiC*H*$_2$O), 2.79 (s, CH$_2$Cl), 1.62 (s, C*H*$_2$CH$_2$CH$_2$Si), 1.30 (s, (CH$_2$)$_6$), 1.14 (s, CH$_2$C*H*$_2$CH$_2$Si), 0.58 (s, CH$_2$CH$_2$C*H*$_2$Si), 0.042 (s, Si(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 75 MHz), δ_{ppm}: 159.4 (inner arom. O*C*$_\mathrm{q}$), 156.8 and 153.0 (outer arom. O*C*$_\mathrm{q}$), 127.5 and 113.8 (arom. *C*H of the dendron), 115.6 and 115.0 (arom. *C*H), 69.0 (O*C*H$_2$(CH$_2$)$_8$), 61.2 (outer Si*C*H$_2$O), 60.8 (inner Si*C*H$_2$O), 43.4 (*C*H$_2$CH$_2$CH$_2$Si), 42.4 (benzylic *C*q), 29.4 and 26.8 (*C*H$_2$)$_6$, 28.7 (CH$_2$Cl), 18.0 (CH$_2$*C*H$_2$CH$_2$Si), 14.9 (CH$_2$CH$_2$*C*H$_2$Si), −4.3 (SiMe$_2$). ^{29}Si NMR (CDCl$_3$, 59.62 MHz), δ_{ppm}: 3.74 (*Si*CH$_2$Cl), 0.29 (*Si*CH$_2$O).

Synthesis of 15. The polyolefin dendrimer **13**[19] (0.050 g, 0.0013 mmol), dry diethyl ether (30 mL), dimethylchloromethylsilane (0.023 g, 0.21 mmol), and Kartsted catalyst (0.1%) were successively introduced into a Schlenk flask under a nitrogen atmosphere. The reaction solution was stirred at 25 °C for 16 h. The solvent was removed under vacuum, the catalyst residue was removed by silica flash chromatography, and the dendrimer was precipitated using dichloromethane/methanol. The dendrimer **15** was obtained as a colorless waxy product in 92% yield (0.056 g).

^{1}H NMR (CDCl$_3$, 300 MHz): 7.19 (d, arom.), 6.78 (d, arom.), 3.83 (t, OC*H*$_2$CH$_2$), 3.49 (s, inner SiC*H*$_2$O), 3.43 (s, outer SiC*H*$_2$O), 2.79 (s, CH$_2$Cl), 1.62 (s, C*H*$_2$CH$_2$CH$_2$Si), 1.25 (s, (CH$_2$)$_6$), 1.11 (s, CH$_2$C*H*$_2$CH$_2$Si), 0.53 (s, CH$_2$CH$_2$C*H*$_2$Si), 0.042 (s, Si(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 75 MHz), δ_{ppm}: 159.3 (inner arom. O*C*$_\mathrm{q}$), 156.8 and 153.0 (outer arom. O*C*$_\mathrm{q}$), 127.5 and 113.7 (arom. *C*H of the dendron), 115.4 and 114.9 (arom. *C*H), 69.1 (O*C*H$_2$(CH$_2$)$_8$), 61.1 (outer Si*C*H$_2$O), 60.8 (inner Si*C*H$_2$O), 43.3 (*C*H$_2$CH$_2$CH$_2$Si), 42.2 (benzylic *C*q), 29.4 and 26.8 (*C*H$_2$)$_6$, 28.7 (CH$_2$Cl), 17.7 (CH$_2$*C*H$_2$CH$_2$Si), 14.9 (CH$_2$CH$_2$*C*H$_2$Si), −4.3 (SiMe$_2$). ^{29}Si NMR (CDCl$_3$, 59.62 MHz), δ_{ppm}: 3.74 (*Si*CH$_2$Cl), 0.29 (*Si*CH$_2$O).

Synthesis of 16. The dendrimer **14** (0.050 g, 0.0033 mmol), NaI (0.027 g, 0.18 mmol), and butanone (50 mL) were successively introduced into a Schlenk flask. The reaction solution was stirred at 80 °C for 16 h. The solvent was removed under vacuum, dissolved in dichloromethane, and washed with an aqueous solution of sodium thiosulphate and with water. The organic solution was dried with sodium sulfate, filtered, and solvent was removed under vacuum. The dendrimer was precipitated using dichloromethane/methanol. The dendrimer **16** was obtained as a colorless waxy product in 96% yield (0.053 g).

^{1}H NMR (CDCl$_3$, 300 MHz): 7.22 (d, arom.), 7.09 (d, arom. core), 6.90 (d, arom.), 3.87 (t, OC*H*$_2$CH$_2$), 3.52 (s, inner SiC*H*$_2$O), 3.46 (s, outer SiC*H*$_2$O), 1.91 (s, CH$_2$I), 1.62 (s, C*H*$_2$CH$_2$CH$_2$Si), 1.30 (s, (CH$_2$)$_6$), 1.14 (s, CH$_2$C*H*$_2$CH$_2$Si), 0.58 (s, CH$_2$CH$_2$C*H*$_2$Si), 0.042 (s, Si(C*H*$_3$)$_2$).

Synthesis of 17. The dendrimer **15** (0.050 g, 0.0011 mmol), NaI (0.026 g, 0.17 mmol), and butanone (50 mL) were successively introduced into a Schlenk flask. The reaction solution was stirred at 80 °C for 16 h. The solvent was removed under vacuum, dissolved in dichloromethane, and washed with an aqueous solution of sodium thiosulphate and with water. The organic solution was dried with sodium sulfate, filtered, and solvent was removed under vacuum. The dendrimer was precipitated using dichloromethane/methanol. The dendrimer **17** was obtained as a colorless waxy product in 91% yield (0.054 g).

^{1}H NMR (CDCl$_3$, 300 MHz): 7.19 (d, arom.), 6.78 (d, arom.), 3.83 (t, OC*H*$_2$CH$_2$), 3.49 (s, inner SiC*H*$_2$O), 3.43 (s, outer SiC*H*$_2$O), 2.79 (s, CH$_2$Cl), 1.91 (s, CH$_2$I), 1.62 (s, C*H*$_2$CH$_2$CH$_2$Si), 1.25 (s, (CH$_2$)$_6$), 1.11 (s, CH$_2$C*H*$_2$CH$_2$Si), 0.53 (s, CH$_2$CH$_2$C*H*$_2$Si), 0.042 (s, Si(C*H*$_3$)$_2$).

Synthesis of 18. The 27-iodomethylsilyl dendrimer **16** (0.050 g, 0.0028 mmol), 4-cyanophenol (0.018 g, 0.15 mmol), and K$_2$CO$_3$ (0.107 g, 0.77 mmol) were introduced into a Schlenk flask, and dry DMF (20 mL) was added. The reaction mixture was stirred at 80 °C, for 48 h. The DMF was removed, 20 mL of CH$_2$Cl$_2$ were added, and the solution was filtered on celite to remove the K$_2$CO$_3$. The solvent was removed in vacuo, and the product was washed with methanol to remove the excess starting material. The product was precipitated twice with dichloromethane/methanol, and **18** was obtained as a colorless waxy product in 87% yield (0.043).

^{1}H NMR (CDCl$_3$, 300 MHz): 7.56 and 6.98 (d, arom. of benzonitrile), 7.22 (d, arom.) and 6.78 (d, arom.), 3.83 (t, OC*H*$_2$CH$_2$), 3.60, 3.48 and 3.43 (s, SiC*H*$_2$O), 1.63 (s, C*H*$_2$CH$_2$CH$_2$Si), 1.26 (s, (CH$_2$)$_6$), 1.11 (s, CH$_2$C*H*$_2$CH$_2$Si), 0.56 (s, CH$_2$CH$_2$C*H*$_2$Si), 0.073 (s, Si(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 75 MHz), δ_{ppm}: 164.8 (*C*$_\mathrm{q}$O of benzonitrile), 158.9 (inner arom. O*C*$_\mathrm{q}$), 155.6 and 152.9 (outer arom. O*C*$_\mathrm{q}$), 133.7 and 114.8 (arom. *C*H of benzonitrile), 127.1 and 113.3 (arom. *C*H of the dendron), 119.4 (*C*≡N), 115.1 (arom. *C*H), 68.6 (O*C*H$_2$(CH$_2$)$_8$), 60.9 (Si*C*H$_2$O), 42.9 (*C*H$_2$CH$_2$CH$_2$Si), 41.9 (benzylic *C*q), 29.4 and 26.8 (*C*H$_2$)$_6$, 17.6 (CH$_2$*C*H$_2$CH$_2$Si), 14.5 (CH$_2$CH$_2$*C*H$_2$Si), −4.7 (SiMe$_2$). Anal. Calcd for $C_{1017}H_{1569}N_{27}O_{90}Si_{63}$: C 70.27, H 9.10. Found: C 69.84, H 9.05. Infrared: $\nu_{\mathrm{CN}} = 2\ 224$ cm^{-1}.

Synthesis of 19. The 81-iodomethylsilyl dendrimer **17** (0.077 g, 0.0014 mmol), 4-cyanophenol (0.027 g, 0.23 mmol), and K$_2$CO$_3$ (0.159 g, 1.13 mmol) were introduced into a Schlenk flask, and dry DMF (20 mL) was added. The reaction mixture was stirred at 80 °C for 48 h. The DMF was removed, 20 mL of CH$_2$Cl$_2$ were added, and the solution was filtered on celite to remove the K$_2$CO$_3$. The solvent was removed in vacuo, and the product was washed with methanol to remove the excess starting material. The product was precipitated twice with dichloromethane/methanol, and **19** was obtained as a colorless waxy product in 83% yield (0.063).

^{1}H NMR (CDCl$_3$, 300 MHz): 7.55 and 6.98 (d, arom. of benzonitrile), 7.22 (d, arom.) and 6.80 (d, arom.), 3.84 (t, OC*H*$_2$CH$_2$), 3.61, 3.49 and 3.43 (s, SiC*H*$_2$O), 1.66 (s, C*H*$_2$CH$_2$CH$_2$Si), 1.25 (s, (CH$_2$)$_6$), 1.14 (s, CH$_2$C*H*$_2$CH$_2$Si), 0.59 (s, CH$_2$CH$_2$C*H*$_2$Si), 0.042 (s, Si(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 75 MHz), δ_{ppm}: 164.7 (*C*$_\mathrm{q}$O of benzonitrile), 158.9 (inner arom. O*C*$_\mathrm{q}$), 155.5 and 152.9 (outer arom. O*C*$_\mathrm{q}$), 133.7 and 114.5 (arom. *C*H of benzonitrile), 127.1 and 113.3 (arom. *C*H of the dendron), 119.2 (*C*≡N), 115.1 (arom. *C*H), 68.4 (O*C*H$_2$(CH$_2$)$_8$), 60.8 (Si*C*H$_2$O), 42.9 (*C*H$_2$CH$_2$CH$_2$Si), 41.9 (benzylic *C*q), 29.4 and 26.8 (*C*H$_2$)$_6$, 17.8 (CH$_2$*C*H$_2$CH$_2$Si), 14.5 (CH$_2$CH$_2$*C*H$_2$Si), −4.7 (SiMe$_2$). Anal. Calcd for $C_{3150}H_{4863}N_{81}O_{279}Si_{198}$: C 70.20, H 9.09. Found: C 69.42, H 9.01. Infrared: $\nu_{\mathrm{CN}} = 2\ 224$ cm^{-1}.

Synthesis of 20. The metallodendrimer **20** was synthesized from **1** (0.028 g, 0.078 mmol), dppe (0.031 g, 0.078 mmol), and dendri-27-CN **18** (0.050 g, 0.0029 mmol) following the general procedure for photochemical reactions. The dendrimer **20** was precipitated with dichloromethane/methanol and was obtained as a red waxy product in 95% yield (0.097 g).

^{1}H NMR (CD$_3$COCD$_3$, 300 MHz): 8.09, 7.59 and 7.19 (m, arom. C*H* of dppe), 7.12 and 6.55 (d, arom. of benzonitrile), 6.84 (s, arom.), 4.62 (s, C*H* of Cp), 3.86 (t, OC*H*$_2$CH$_2$), 3.76, 3.67 and 3.49 (s, SiC*H*$_2$O), 1.71 (s, C*H*$_2$CH$_2$CH$_2$Si), 1.29 (s, (CH$_2$)$_6$), 1.19 (s, CH$_2$C*H*$_2$CH$_2$Si), 0.62 (s, CH$_2$CH$_2$C*H*$_2$Si), 0.014, 0.093 and 0.042 (s, Si(C*H*$_3$)$_2$). ^{13}C NMR (CD$_3$COCD$_3$, 75.0 MHz): 166.1 (*C*$_\mathrm{q}$O of benzonitrile), 160.0 (inner arom. $\mathrm{O}C_{\mathrm{q}}$), 156.6 and 154.1 (outer arom. $\mathrm{O}C_{\mathrm{q}}$), 140.9–126.0 (arom. of dppe and *C*H of benzonitrile), 116.0 and 115.7 (*C*H, arom.), 114.4 ($C{\equiv}\mathrm{N{-}Fe}$), 104.4 and 103.7 (C_{q}, arom.), 80.5 (*C*H of Cp), 69.1 ($\mathrm{O}C\mathrm{H_2(CH_2)_8}$), 61.7 and 61.5 ($\mathrm{Si}C\mathrm{H_2O}$), 55.2 ($\mathrm{P(CH_2)_2P}$), 43.9 ($C\mathrm{H_2CH_2CH_2Si}$), 42.4 (benzylic C_{q}), 29.8 and 26.8 ($(C\mathrm{H_2})_6$), 18.6 ($\mathrm{CH_2}C\mathrm{H_2CH_2Si}$), 15.5 ($\mathrm{CH_2CH_2}C\mathrm{H_2Si}$), −4.0 ($\mathrm{SiMe_2}$). ^{31}P NMR ($\mathrm{CH_3COCH_3}$, 121 MHz): 97.37 ($\mathrm{Fe^+}$-*P*), 126.7–161.6 ($\mathrm{PF_6}$). Infrared: $\nu_{\mathrm{CN}} = 2221$ cm^{-1}, $\nu_{\mathrm{PF_6}} = 838$ cm^{-1}. Anal. Calcd for $\mathrm{C_{1854}H_{2352}N_{27}F_{162}Fe_{27}O_{90}P_{81}Si_{63}}$: C 63.05, H 6.71. Found: C 63.86, H 6.87.

Synthesis of 21. The metallodendrimer **21** was synthesized from **1** (0.016 g, 0.045 mmol), dppe (0.018 g, 0.045 mmol), and dendri-81-CN **19** (0.030 g, 0.00055 mmol) following the general procedure for photochemical reactions. The dendrimer **20** was precipitated with dichloromethane/methanol and was obtained as a red waxy product in 92% yield (0.053 g).

^{1}H NMR ($\mathrm{CD_3COCD_3}$, 300 MHz): 8.06, 7.53 and 7.20 (m, arom. C*H* of dppe), 7.12 and 6.57 (d, arom. of benzonitrile), 6.80 (s, arom.), 4.60 (s, C*H* of Cp), 3.85 (t, $\mathrm{OC}H_2\mathrm{CH_2}$), 3.66 and 3.49 (s, $\mathrm{SiC}H_2\mathrm{O}$), 1.69 (s, $\mathrm{C}H_2\mathrm{CH_2CH_2Si}$), 1.29 (s, $\mathrm{(CH_2)_6}$), 1.19 (s, $\mathrm{CH_2C}H_2\mathrm{CH_2Si}$), 0.61 (s, $\mathrm{CH_2CH_2C}H_2\mathrm{Si}$), 0.044 (s, $\mathrm{Si(C}H_3\mathrm{)_2}$). ^{13}C NMR ($\mathrm{CH_3COCH_3}$, 75.0 MHz): 166.0 ($C_{\mathrm{q}}\mathrm{O}$ of benzonitrile), 159.7 (inner arom. $\mathrm{O}C_{\mathrm{q}}$), 156.6 and 154.1 (outer arom. $\mathrm{O}C_{\mathrm{q}}$), 140.9–126.0 (arom. of dppe and *C*H of benzonitrile), 116.1 and 115.6 (*C*H, arom.), 114.3 ($C{\equiv}\mathrm{N{-}Fe}$), 104.4 and 103.7 (C_{q}, arom.), 80.4 (*C*H of Cp), 69.1 ($\mathrm{O}C\mathrm{H_2(CH_2)_8}$), 61.5 ($\mathrm{Si}C\mathrm{H_2O}$), 55.2 ($\mathrm{P(CH_2)_2P}$), 43.7 ($C\mathrm{H_2CH_2CH_2Si}$), 42.2 (benzylic C_{q}), 29.8 and 26.8 ($(C\mathrm{H_2})_6$), 18.6 ($\mathrm{CH_2}C\mathrm{H_2CH_2Si}$), 15.3 ($\mathrm{CH_2CH_2}C\mathrm{H_2Si}$), −4.1 ($\mathrm{SiMe_2}$). ^{31}P NMR ($\mathrm{CH_3COCH_3}$, 121 MHz): 97.37 ($\mathrm{Fe^+}$-*P*), 126.5–161.6 ($\mathrm{PF_6}$). Infrared: $\nu_{\mathrm{CN}} = 2221$ cm^{-1}, $\nu_{\mathrm{PF_6}} = 838$ cm^{-1}. Anal. Calcd for $\mathrm{C_{5661}H_{7212}N_{81}F_{486}Fe_{81}O_{90}P_{243}Si_{198}}$: C 64.95, H 6.94. Found: C 65.76, H 6.98.

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Supporting Information Available: Cyclo-voltammograms of complexes **3**−**6** and ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra of the organic and organoiron compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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