# Inorganic Chemistry

Article

# From Simple Monopyridine Clusters [Mo₆Br₁₃(Py-R)][*n*-Bu₄N] and Hexapyridine Clusters [Mo₆X₈(Py-R)₆][OSO₂CF₃]₄ (X = Br or I) to Cluster-Cored Organometallic Stars, Dendrons, and Dendrimers

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Hexasubstitution of apical triflate ligands in the octahedral clusters [M]₂[Mo₆X₈(CF₃SO₃)₆] (M = *n*-Bu₄N or Cs, X = Br or I) and monosubstitution in [*n*-Bu₄N]₂[Mo₆Br₁₃(CF₃SO₃)] was carried out in tetrahydrofuran at 60 °C with simple pyridines and then extended to organometallic pyridines, yielding cluster-cored stars, and to dendronic polyallyl- and polyferrocenylpyridines, yielding cluster-cored polyallyl and polyferrocenyl dendrimers and dendrons. The orange pyridine-substituted clusters, whose pyridine protons are deshielded in ¹H NMR (a practical tool for characterization), are air-stable and thermally stable with simple pyridines, light- and air-sensitive with organometallic pyridines, and air-fragile and thermally fragile with large dendronized pyridines.

## Introduction

Octahedral clusters have been shown by Zheng's group[1] with hexarhenium selenides to serve as versatile building blocks for the synthesis of various architectures including dendrimers,[1b,2] and coordination networks with structures constructed from hexatungsten sulfides have been disclosed by the DiSalvo group.[3] Other groups have utilized metal clusters for the design of extended molecular arrays,[4] but the two above-mentioned successful examples illustrate the

potential of octahedral hexametallic clusters to be used as starting points for the synthesis of molecular assemblies and nanosized materials with catalytic and unusual physical properties.[5] Among these clusters based on early-transition elements, the hexamolybdenum series built up from [Mo₆X₁₄]²⁻ units (X = Cl, Br, I) constitute relevant starting materials easily available from inorganic solids that have been structurally characterized 60 years ago.[6] The octahedral molybdenum clusters became most popular when the superconducting properties of the related chalcogenides MₓMo₆Y₈ (Y = chalcogen), known as Chevrel phases, were discovered.[7] Photophysical and redox properties of [Mo₆X₁₄]²⁻ added further interest.[8] Among the 14 halide ligands, the 8

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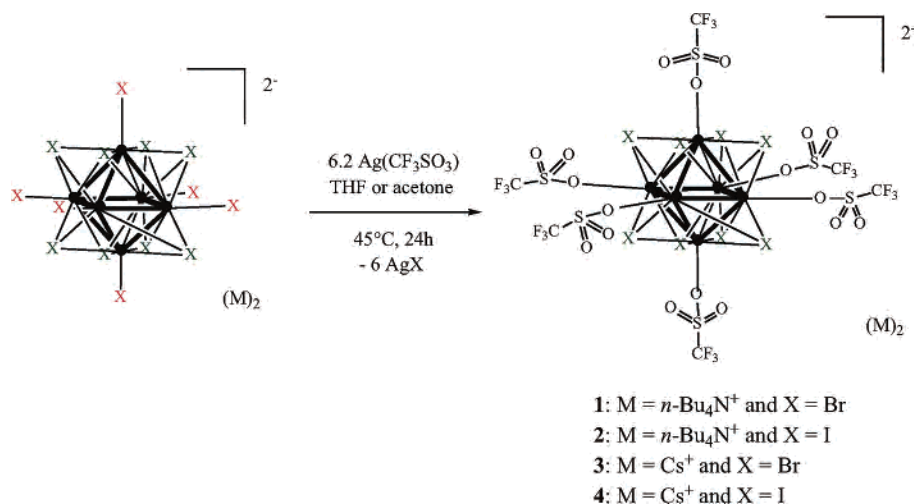  † Université Bordeaux 1.
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**Scheme 1**



**1**: M = *n*-Bu$_4$N$^+$ and X = Br
**2**: M = *n*-Bu$_4$N$^+$ and X = I
**3**: M = Cs$^+$ and X = Br
**4**: M = Cs$^+$ and X = I

face-capping ones are relatively unreactive, which makes resistant cluster cores [Mo$_6$X$_8$]$^{4+}$. In the case of [Mo$_6$Cl$_{14}$]$^{2-}$ units, the inner chloride ligands can be replaced by chalcogen ligands, a soft route to Chevrel phases. The substitution of the six semilabile apical ligands in [Mo$_6$X$_{14}$]$^{2-}$ can be achieved easily and leads to various [Mo$_6$Y$_8$L$_6$] clusters,[9] which have been examined for a long time.[10] In particular, the hexamethoxy clusters [Mo$_6$Br$_8$(OMe)$_6$]$^{2-}$, reported by Nannelli and Block,[11] and the hexatriflate clusters [Mo$_6$Br$_8$(OSO$_2$CF$_3$)$_6$]$^{2-}$, reported by Shriver et al.,[4c,12] are the most useful starting materials for further substitution.

We have investigated mono- and hexapyridine complexes of the [Mo$_6$Br$_8$]$^{4+}$ and [Mo$_6$I$_8$]$^{4+}$ cores by simple substitution of the triflate ligands in Shriver's complex [Mo$_6$Br$_8$(OSO$_2$CF$_3$)$_6$]$^{2-}$ and its homologue [Mo$_6$I$_8$(OSO$_2$-CF$_3$)$_6$]$^{2-}$, to further assemble functional mono- and hexapyridine Mo$_6$ complexes into dendritic and nanoscopic structures. The synthetic findings are reported here. Although

hexapyridine hexametallic clusters are known with the [Re$_6$Se$_8$]$^{2+}$,[1,13] W$_6$S$_8$,[14] and Mo$_6$S$_8$[9b] cluster series, there is no report with the [Mo$_6$X$_8$]$^{4+}$ core. Some 4,4′-bipyridine complexes have been reported by Shriver's group, however, in the chloro series.[15a] Our investigation is extended to pyridines substituted by transition-metal groups and to dendronic pyridines including ferrocenyl dendronic pyridines. Metal-cluster-cored dendrimers have already been reported by Gorman[5f,16a] with the biomimetic Fe$_4$S$_4$ core and by Zheng[1,13] with the Re$_6$L$_8$$^{2+}$ cores (L = S, Se).

## Results and Discussion

**A. Cluster Hexasubstitution. Hexatriflate Clusters.** Shriver-type hexatriflate clusters [M]$_2$[Mo$_6$X$_8$(CF$_3$SO$_3$)$_6$] **1**–**4** serve as starting points. They are prepared by reactions of the clusters Mo$_6$X$_{14}$M$_2$ and silver triflate, a reaction that is carried out in tetrahydrofuran (THF) at 45 °C for 24 h in the case of [M]$_2$[Mo$_6$X$_8$(CF$_3$SO$_3$)$_6$] (M = *n*-Bu$_4$N or Cs). Starting from the clusters Cs$_2$Mo$_6$X$_{14}$ (X = Br or I) that are insoluble in THF, the clusters [Cs]$_2$[Mo$_6$X$_8$(CF$_3$SO$_3$)$_6$], **3** (X = Br) and **4** (X = I), are synthesized according to the substitution reaction that is carried out in acetone at 45 °C for 24 h (and the resulting clusters **3** and **4** are THF-soluble). The clusters **1**–**4** are purified by simple filtration of the reaction mixture on Celite under an inert atmosphere in order to remove AgX, and the yields are virtually quantitative (Scheme 1).
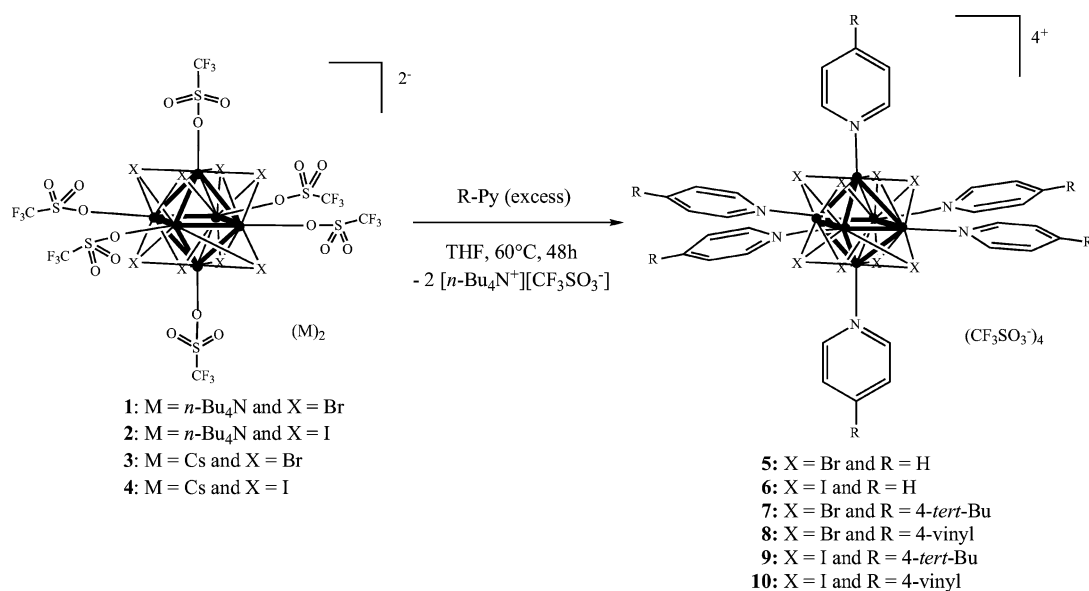
**Clusters 5–10 Hexasubstituted with Simple Pyridines.** The substitution reaction of the six triflate ligands with six pyridine ligands in the complexes **1**–**4** is completed in 2 days at 60 °C in pyridine/THF (Scheme 2). The reaction is followed by $^1$H NMR by comparison of the intensities of
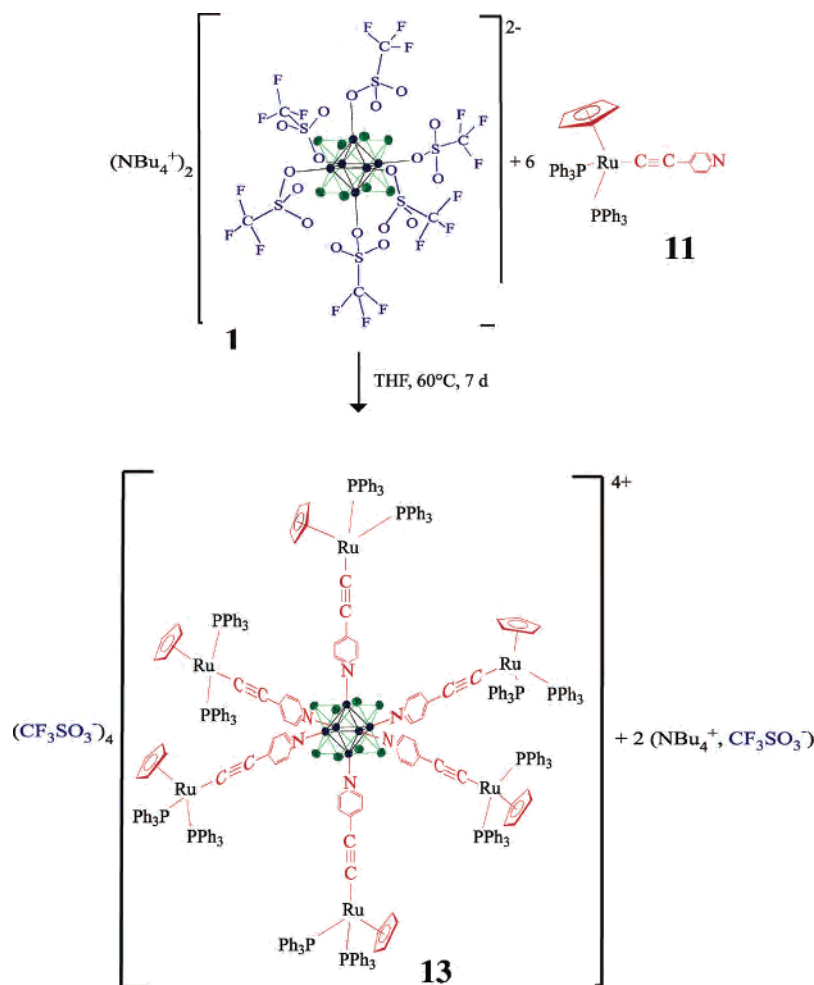
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**Scheme 2**



1: M = *n*-Bu₄N and X = Br
2: M = *n*-Bu₄N and X = I
3: M = Cs and X = Br
4: M = Cs and X = I

5: X = Br and R = H
6: X = I and R = H
7: X = Br and R = 4-*tert*-Bu
8: X = Br and R = 4-vinyl
9: X = I and R = 4-*tert*-Bu
10: X = I and R = 4-vinyl

**Scheme 3**



the pyridine protons with those of the tetrabutylammonium countercation. In the pyridine-substituted clusters, the pyridine protons are all deshielded compared to free pyridine. For example, this deshielding effect is most marked for the ortho-substituted pyridine protons moving from 8.41 ppm vs tetramethylsilane (TMS) in CDCl₃ in free pyridine to 8.76 ppm in **5**. From the yellow starting cluster **1**, the new orange complex **5** precipitates from the reaction medium. The triflate salt [*n*-Bu₄N][CF₃SO₃] is thus readily separated because it is soluble in THF, and the orange solid product **5** is washed with THF. It is sparingly soluble in dichloromethane and chloroform. It is insoluble in pyridine, ether, THF, and

**Scheme 4**
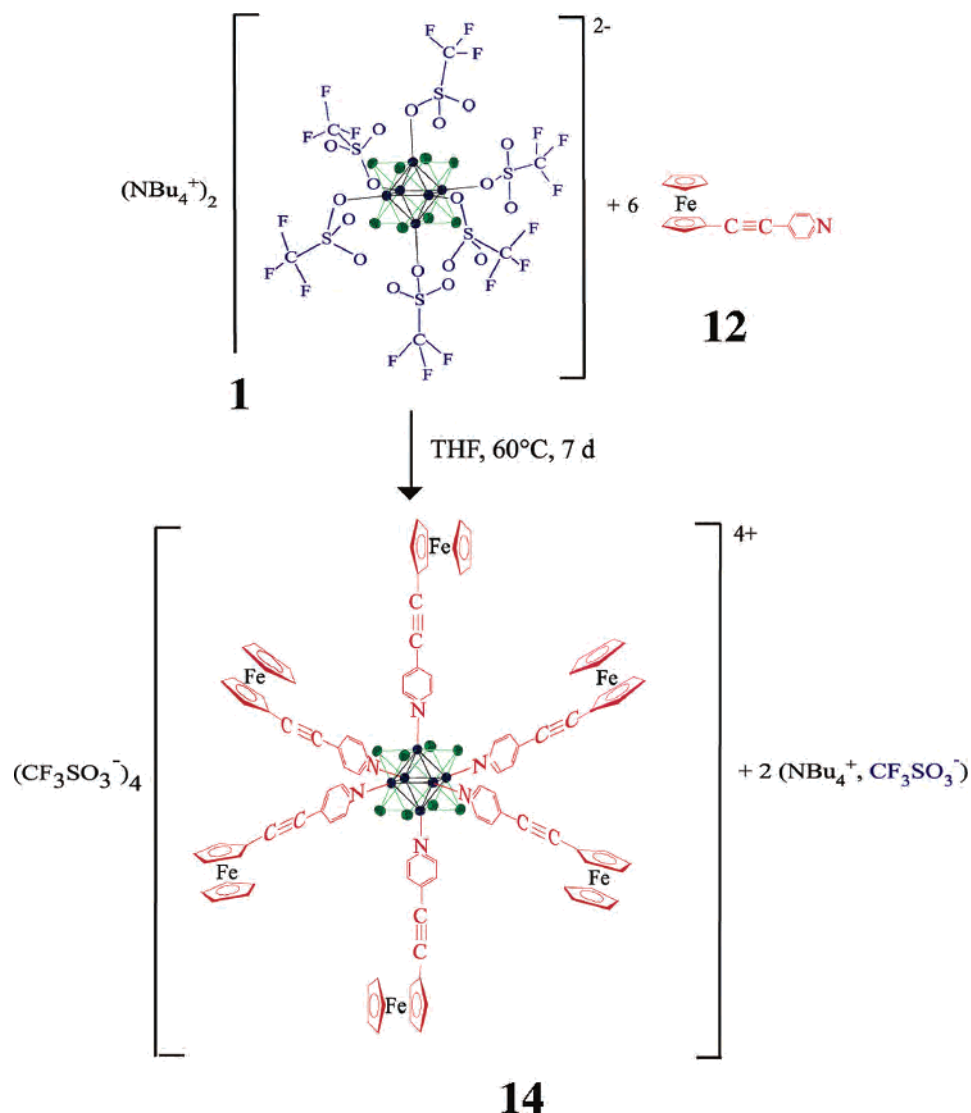


alkanes, and it decomposes in methanol and water. The cluster **5** is air-stable even in acetone and in the presence of light. The same remarks apply to the synthesis of the cluster **6**. The ortho-substituted pyridine protons are shifted in $^1$H NMR from 8.41 ppm vs TMS in $CDCl_3$ for free pyridine to 8.70 ppm for **6**, and the solubility properties are the same for **5** and **6**. The isolated reaction yields are 79% for **5** and 76% for **6** (Scheme 2). The reactivity and yields are seemingly not influenced by the nature of the countercation, $Cs^+$ or $n$-$Bu_4N^+$, but the reaction cannot be followed by $^1$H NMR with the cesium salt (the relative intensities of the coordinated and free pyridine signals can be compared, however).

Ligand substitution of **1**−**4** with para-substituted pyridines was conducted in THF at 60 °C using about a 100-fold excess of para-substituted pyridine, i.e., in pyridine/THF solvents, and the reactions lasted 2 days (Scheme 2). Reactions were monitored analogously by comparing the intensity of the tetrabutylammonium $^1$H NMR peaks with those of the ortho protons of the pyridine ligands. No precipitate formed, with the orange solution remaining homogeneous at the end of the reaction with 4-*tert*-butylpyridine. The separation of

$[n$-$Bu_4N][CF_3SO_3]$ from the new clusters **7** and **9** is tedious because these clusters are now much more soluble in a variety of solvents such as pyridine and THF. It proceeds by successive precipitations from acetone by controlled addition of pentane and is checked by $^1$H NMR. Several such reprecipitations are required in order to remove the salt. Thus, finally, removal of this salt is only complete with the approximation of the $^1$H NMR accuracy of ca. 98%. Elemental analyses show carbon contents that are often low, presumably because of the presence of this and/or other extra salts in analyzed samples. Again, the orange cluster compounds obtained are air- and light-stable even in solution for at least several hours. They are unstable in water. For **8** and **10**, a precipitate forms in the course of the reaction. Simple washing with pentane and THF then purifies the clusters. The yields are analogous whatever the halide ligands in the cluster, the nature of the countercation seemingly does not influence the reactions, and the color slightly varies from orange for the bromo clusters to dark orange for the iodo clusters.

**Clusters 13 and 14 Hexasubstituted by Organometallic Pyridines.** We synthesized the known rigid organoruthenium

**Scheme 5**



**17**
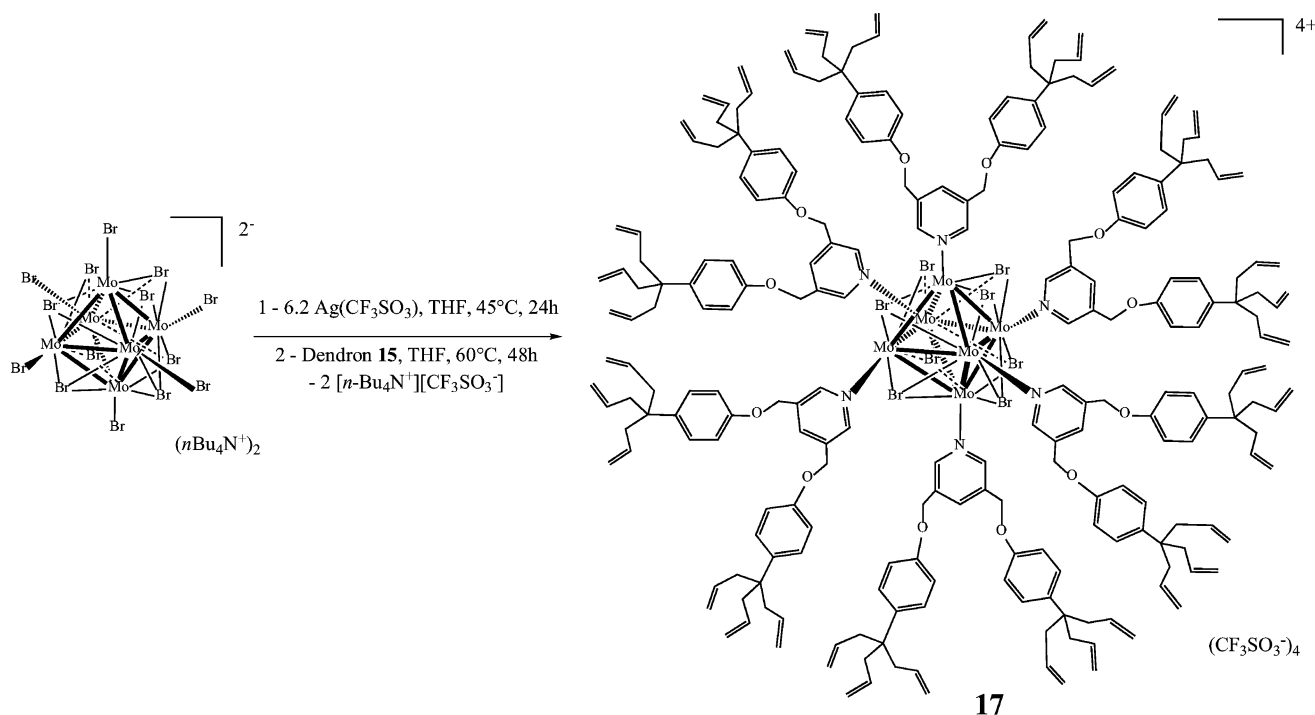
pyridine ligand **11**[17] by a new route involving the reaction of commercial 4-ethynylpyridine hydrochloride with [RuCp-(PPh$_3$)$_2$Cl] in the presence of triethylamine and [NH$_4$][PF$_6$] in methanol. This general procedure was reported for the synthesis of the complexes [RuCp(PPh$_3$)$_2$($\eta^1$-alkynyl)] with (Cp = $\eta^5$-C$_5$H$_5$).[18,19] The yellow complex **11** was characterized by standard spectroscopic techniques including $^{31}$P NMR, infrared spectroscopy ($\nu_{CC}$ = 2070 cm$^{-1}$), and the MALDI TOF mass spectrum with the dominant molecular peak at 794 Da. The reaction of **11** with the cluster [Mo$_6$Br$_8$(CF$_3$SO$_3$)$_6$][$n$-Bu$_4$N]$_2$, **1**, was carried out in refluxing THF for 1 week (Scheme 3).

The new hexaruthenium hexamolybdenum cluster **13** was recovered by slow precipitation using pentane. A single peak was found in the $^{31}$P NMR spectrum, a single Cp peak was observed in the $^1$H NMR spectrum at $\delta$ = 4.42 ppm, and a single infrared absorption was obtained at $\nu_{CC}$ = 2018 cm$^{-1}$. This behavior is in accord with the coordination of the cluster by the six organoruthenium pyridine ligands and the absence of a free pyridine ligand in the sample.

In a similar approach, the red complex 1-ferrocenyl-2-(4-pyridinyl)acetylene **12** was synthesized using the reaction of Vargas' group.[20] The reaction of the ferrocenyl-containing pyridinyl ligand **12** with the cluster **1** was carried out in refluxing THF for 1 week to give the new hexasubstituted hexaferrocenyl Mo$_6$ cluster **14** (Scheme 4). The red com-

pound **14** was isolated by precipitation from a THF solution by slow addition of pentane and characterized inter alia by an infrared alkynyl absorption at 2181 cm$^{-1}$, with ferrocene signals including a single Cp signal for the free Cp rings in the $^1$H and $^{13}$C NMR spectra. This complex **14** is very light- and air-sensitive. Its cyclic voltammogram (CV) in CH$_2$Cl$_2$ shows two close reversible ferrocenyl waves at $E_{1/2}$ = 0.800 V vs [FeCp*$_2$] with a less intense shoulder at $E_{1/2}$ = 0.710 V vs [FeCp*$_2$]; these values compare with the value obtained for the starting monomeric complex **12**, $E_{1/2}$ = 0.720 V vs [FeCp*$_2$]. Thus, it is probable that this shoulder does correspond to some decoordinated monoferrocenyl ligand formed in the electrochemical cell.

**Cluster-Cored Dendrimers 17 and 18: Hexasubstitution by Dendronic Pyridines.** The dendronic pyridine 3,3′-py{CH$_2$O-$p$-C$_6$H$_4$C(CH$_2$CH=CH$_2$)$_3$}$_2$, **15**, is synthesized by the reaction of 3,3′-py(CH$_2$Br)$_2$[22] with the phenol dendron HO-$p$-C$_6$H$_4$C(CH$_2$CH=CH$_2$)$_3$.[23] The reaction of **15** with **1** was carried out for 6 days in refluxing THF using 6.2 equiv of dendron **15** to give the orange cluster **17** (Scheme 5). The $^1$H NMR spectra show that the reaction is complete from the relative intensity ratio between the ammonium protons and the coordinated pyridine protons. Indeed, the para-substituted pyridine proton is deshielded from 7.95 ppm in free pyridine to 8.66 ppm in the coordinated pyridine dendron. The solution is orange at the end of the reaction, and the reaction time is seemingly not longer than that with

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**Scheme 6**
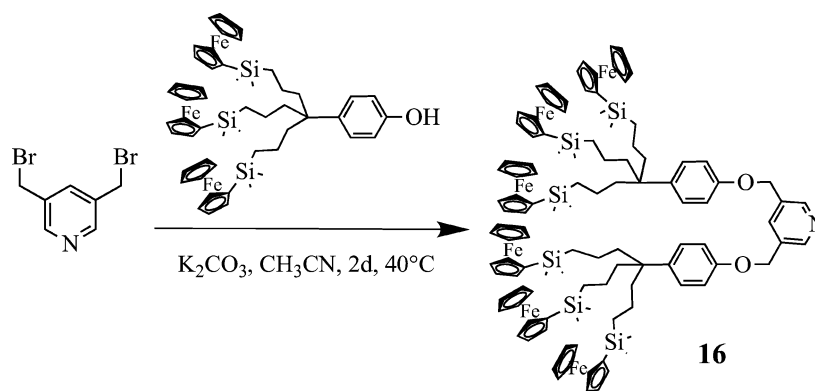


**Scheme 7**



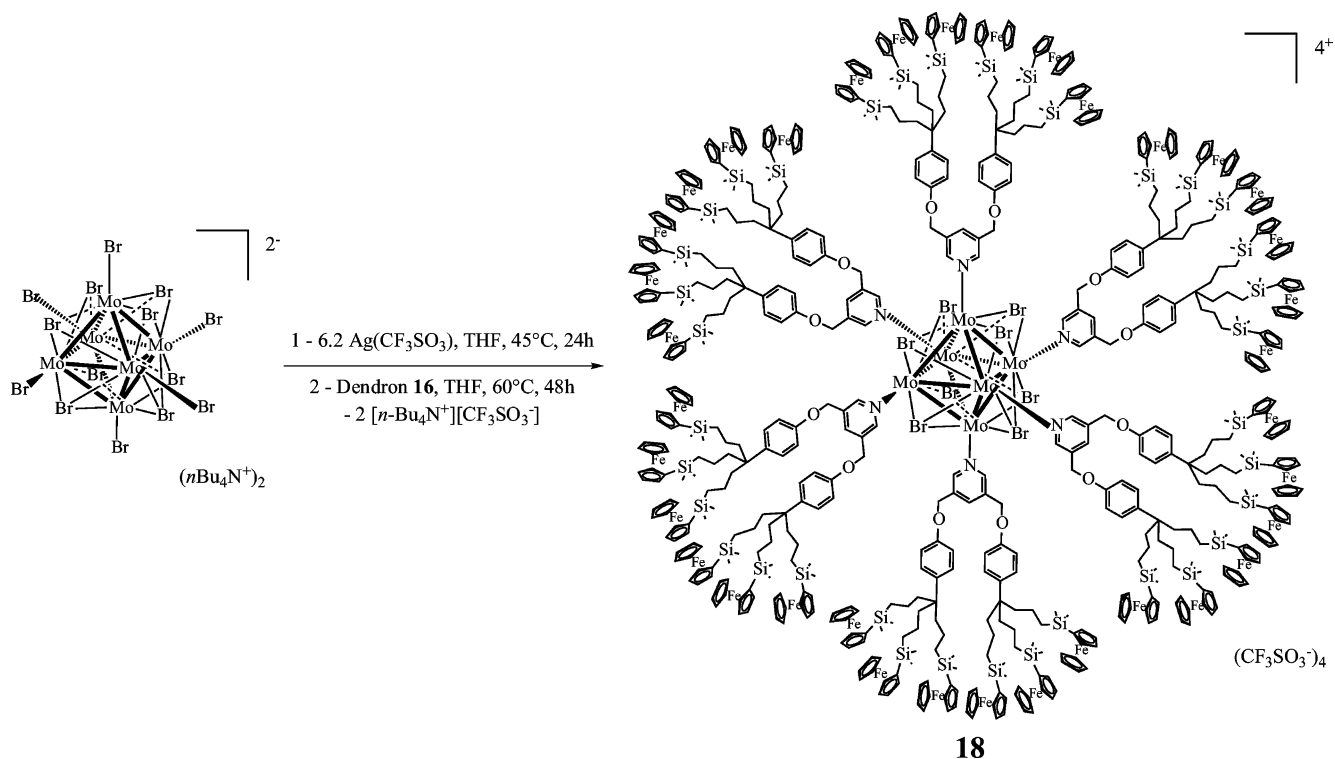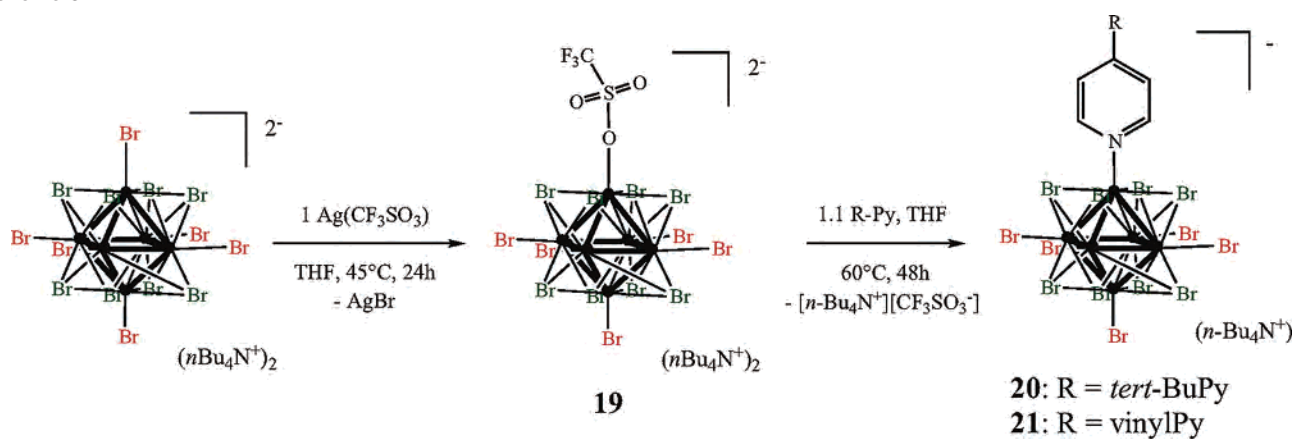the other pyridines, as monitored by ^{1}H NMR. After numerous reprecipitations in order to remove the salts, the ^{1}H NMR spectrum shows that the ammonium salt is no longer present and the carbon content in the elemental analysis of the cluster-cored dendrimer **17** is acceptable. The orange compound **17** is soluble in dichloromethane and air- and light-stable in this solvent; however, it is insoluble in pentane. After 1 day in a chloroform solution under an inert atmosphere, the solution is still orange, but some decomposition to an insoluble film is observed. Although the conversion is complete as monitored by ^{1}H NMR, the yield is eventually mediocre because of the repeated precipitations (Scheme 5). Olefin metathesis reactions were attempted at 45 °C in dichloromethane with Grubbs' second-generation commercial catalyst [RuCl₂(=CHPh)(NHC)] (NHC = bis-mesityl N-heterocyclic carbene) with **17**, but all attempts failed presumably because of partial pyridine decoordination and subsequent coordination to the ruthenium of the catalyst, which inhibits metathesis activity.

The dendronic pyridine 3,3′-{CH₂O-*p*-C₆H₄C(CH₂CH₂-CH₂SiMe₂C₅H₅FeCp)₃}₂Py, **16**, is synthesized by the reaction of the phenol dendron HO-*p*-C₆H₄C(CH₂CH₂CH₂SiMe₂C₅H₅-FeCp)₃ with 3,3′-py(CH₂Br)₂ (Scheme 6).

Reaction of **16** with **1** was carried out for 6 days in refluxing THF using 6.2 equiv of dendron **16** to give the orange cluster **18** (Scheme 7). ^{1}H NMR shows that the reaction is completed from the relative intensity ratio between the ammonium protons and the coordinated pyridine protons. Indeed, the para-substituted pyridine proton is deshielded from 7.91 ppm in free pyridine to 8.50 ppm in the coordinated pyridine dendron. The final solution is orange. After numerous reprecipitations in order to remove the salts, ^{1}H NMR shows that the ammonium salt is no longer present and the carbon content in the elemental analysis of the cluster-cored dendrimer **18** is acceptable. The orange cluster compound **18**, insoluble in pentane, is soluble in dichloromethane, but it is neither air- nor light-stable. Although the conversion is complete as monitored by ^{1}H NMR, the yield

**Scheme 8**



**19**
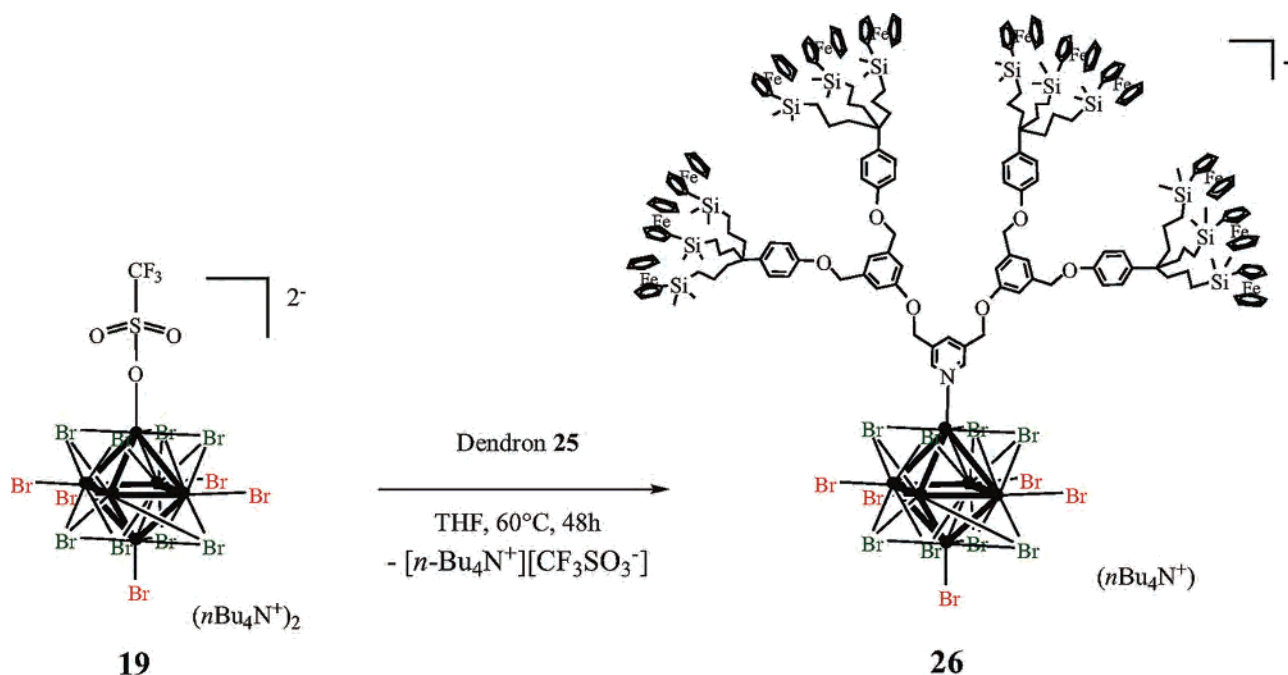
**20**: R = *tert*-BuPy
**21**: R = vinylPy

**Scheme 9**



**22**

LiAlH₄
THF, 6h, reflux

**24**          Br₃P
              4h, DMF          **23**

K₂CO₃
CH₃CN, 2d

**25**
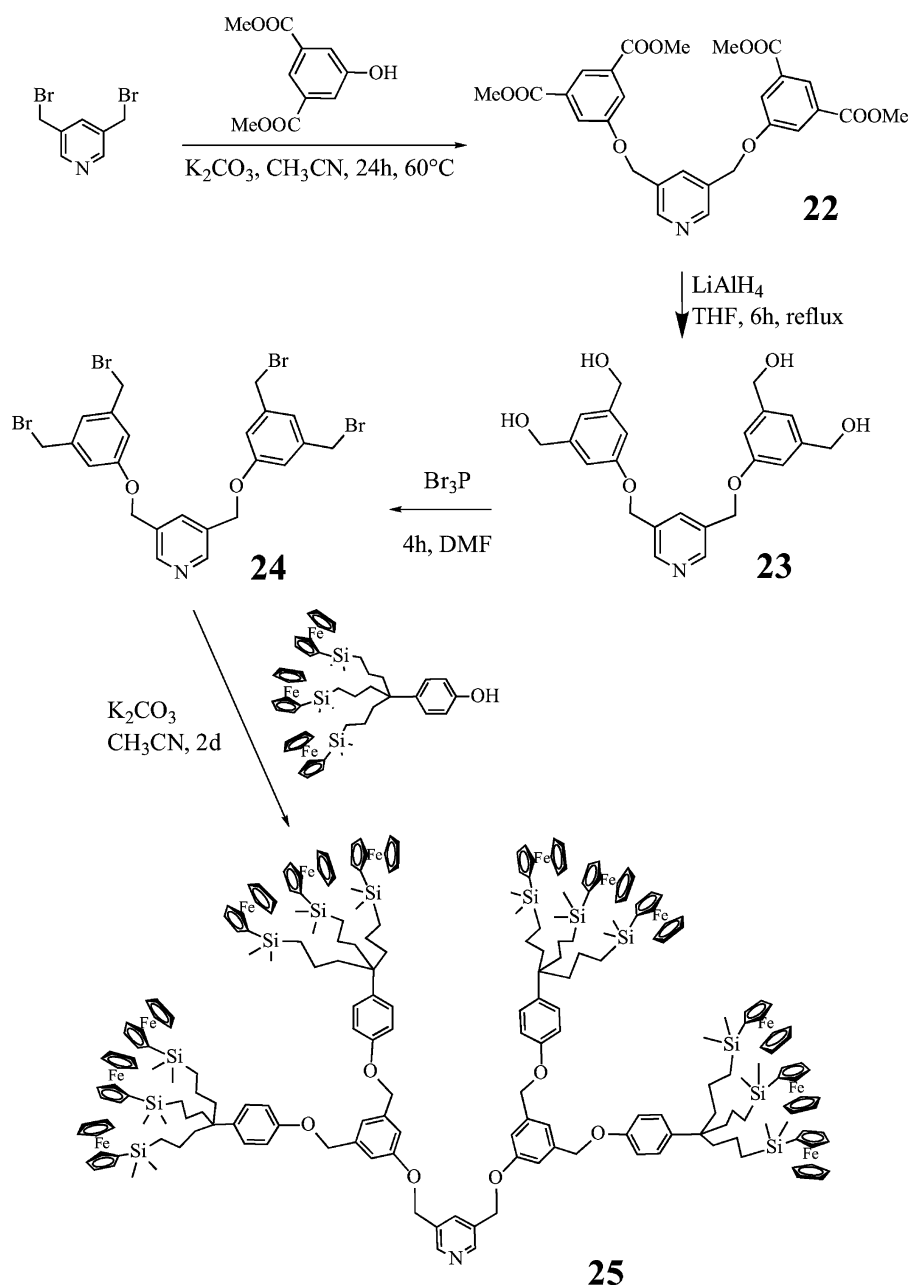
**Scheme 10**



is eventually mediocre because of the repeated precipitations required to purify this cluster-cored dendrimer **18**. The thermal stability of **18** is weak because it decomposes over periods of several days at room temperature under an inert atmosphere.

The CV of a freshly prepared sample of **18** in dichloromethane shows a single reversible wave, indicating that the 36 ferrocenyl centers are seemingly identical and sufficiently remote from one another to render the electrostatic factor negligible. No adsorption was noted under these conditions, allowing the determination of the number of redox-active units by comparison of the current intensity of the cluster wave with that of an internal reference such as decamethylferrocene. The Bard−Anson equation, involving these intensities and the respective molecular weights of the compound and reference,[24] provides a number of ferrocenyl redox centers equal to 37 ± 3, showing a good agreement with the theoretical number of 36.[25]

**B. Cluster Monosubstitution. Clusters Monosubstituted by Simple Pyridines.** Given the progressive substitution of the apical halide ligands in the hexamolybdenum clusters, we investigated the possibility of also synthesizing monosubstituted pyridine clusters in order to eventually introduce a single functional group to derivatize the cluster. In a systematic study of the hexarhenium sulfide clusters, Holm's group could optimize the synthesis of all of the possible substituted clusters.[21] The present hexamolydenum clusters are far from being as air-stable as hexarhenium clusters; therefore, this strategy is much more limited here. In particular, for this reason, chromatographic separation cannot

be envisaged. The monosubstitution reaction of a bromide by a triflate is best performed for 24 h at 45 °C (Scheme 8). Silver triflate is slowly introduced into the reaction medium in order to favor monosubstitution whose yield is virtually quantitative. The monosubstituted triflate cluster **19** is a THF-soluble yellow solid serving as an intermediate for further introduction of a pyridine-type ligand. We have not investigated the compared rates of mono- and disubstitutions, although the yields of monopyridine-substituted products indicate that the second substitution does not occur more rapidly than the first one.

The substitution of the triflate ligand by a pyridine derivative is complete in 2 days at 60 °C in THF (Schemes 8 and 10). This type of reaction is monitored by ^{1}H NMR by comparing the intensities of the signals of the coordinated pyridine with those of the countercation $n$-Bu$_4$N$^+$. Here again, the signals of the pyridine protons are shifted upon coordination to the cluster. The monosubstituted clusters **20** and **21** are orange, and they are much less soluble in common solvents than the hexasubstituted analogues. They precipitate during the reaction; thus, purification is simple by washing the precipitate with pentane and then with THF, followed by filtration on Celite, and ^{1}H NMR analysis is carried out in acetone-$d_6$. The yields are modest (48% for **20** and 37% for **21**), which indicates that disubstitution also simultaneously occurs because of near-statistical substitution. The disubstituted products are neutral, and thus probably well THF-soluble, but were not investigated. With the unsubstituted triflate cluster complex being also THF-soluble, the monopyridine clusters are the only THF-insoluble products among these three compounds (non-, mono-, and disubstituted). Olefin metathesis experiments were carried out with **21** as with **17**, but they were not successful, presumably for the same reason involving some partial decoordination of

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(25) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.
(26) For earlier detailed related work, see: Daniel, M.-C.; Ruiz, J.; Blais, J.-C.; Daro, N.; Astruc, D. *Chem.—Eur. J.* **2003**, *9*, 4371.
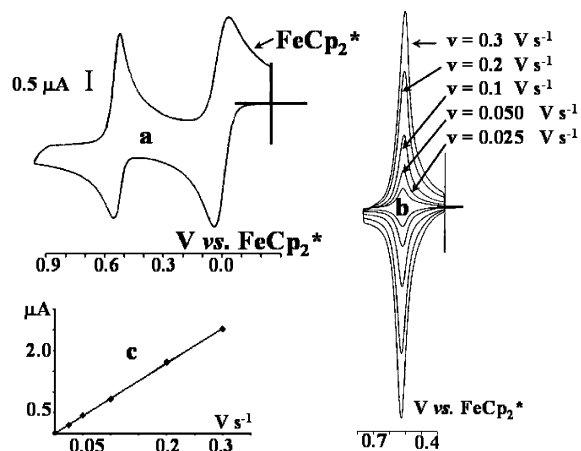
**Figure 1.** CVs of the cluster-cored dendron **26**: solvent, $CH_2Cl_2$; reference electrode, Ag/Ag$^+$; working electrode, none; counter electrode, Pt; supporting electrolyte, 0.1 M $n$-Bu$_4$NPF$_6$; internal reference, FeCp$_2$*; (a) **26** in solution; (b) **26** coated over a Pt electrode at various scan rates ($E_{1/2}$ = 0.53 V vs FeCp$_2$*); (c) inset by **26**. The intensity was as a function of the scan rate. The linearity shows the expected behavior of the modified electrode with full adsorption of **26**. The surface coverage by **26** was determined from the integrated charge of the CV wave. Thus, the surface coverage for the electrode modified with **26** was $\Gamma = 1.3 \times 10^{-10}$ mol cm$^{-2}$ (iron sites), corresponding to $1.08 \times 10^{-11}$ mol cm$^{-2}$ of **26**. The difference between the anodic and cathodic potentials is $\Delta E = E_c - E_a = 0.0$ V, and the full width at half-maximum ($\Delta E_{fwhm}$) is 0.90 V.

the substituted pyridine from the cluster and inhibition of the ruthenium catalyst.

**Ferrocenyl-Dendronized Cluster 26 Monosubstituted by a 12-Ferrocenylpyridine Dendron 25.** The reaction of 1 equiv of **19** with 1 equiv of monopyridine dendron **25** bearing 12 ferrocenyl groups at the periphery (Scheme 9) is also carried out in THF at 60 °C for 2 days and yields the thermally sensitive pentane-soluble orange compound **26** (Scheme 10).

The para-substituted pyridine protons of **26** are found at 8.22 ppm vs TMS in CDCl$_3$ (compared to free pyridine at 7.90 ppm). The solubility of **26** in pentane precludes purification from other pentane-soluble impurities such as the free ligand and, in addition, **26** is not thermally stable at room temperature over a few hours. Thus, its synthesis must be carried out in the presence of only 1 equiv of the dendronic pyridine ligand, whose coordination can be monitored by $^1$H NMR using the signals of the pyridine protons, and indeed coordination is completed. It is possible, however, that some disubstituted compound is present in the reaction mixture.

The CV of a freshly prepared sample of **26** shows a single ferrocenyl wave for the 12 ferrocenyl groups, and application of the Bard–Anson equation[21] leads to a number of redox centers equal to $14 \pm 2$. The error on this measurement is somewhat larger than that in the case of the cluster-cored ferrocenyl dendrimer **18** presumably because of the purity of the sample, which is lower for **26** than for **18**. A modified Pt electrode is prepared with **18** by scanning about 100 times around the ferrocenyl redox potential region, which produced an electrode, giving the CV shown in Figure 1 in which the 0 V difference between $E_{pa}$ and $E_{pc}$ values confirms correct electrode modification. The modified electrode can also

recognize the $n$-Bu$_4$N$^+$ salt of ATP$^{2-}$, and when this salt is added to the electrochemical cell containing the modified electrode, a new reversible wave appears at 90 mV less positive potential.[22]

**Concluding Remarks**

(i) An easy route to a family of new mono- and hexa-pyridine octahedral hexamolybdenum hexapyridine clusters [Mo$_6$X$_8$(4-Py-R)$_6$][CF$_3$SO$_3$]$_4$ has been disclosed starting from the precursor complex [M]$_2$[Mo$_6$X$_{14}$] via the triflate intermediates. The homogeneity of the reaction mixture allows monitoring of their formation by $^1$H NMR by comparison of the relative intensities of the tetrabutylammonium signals and those of the pyridine protons that become deshielded upon pyridine coordination. The use of substituted pyridine largely increases the solubility of the new clusters, which renders the separation of the Mo$_6$ cluster from the salt [$n$-Bu$_4$N][OSO$_2$CF$_3$] difficult with the tetrabutylammonium salt used at the beginning of the synthesis. This separation can be achieved by successive reprecipitations, however.

(ii) Organometallic pyridines could be grafted onto the six apical positions of the cluster, yielding light- and air-sensitive clusters surrounded by organometallic fragments.

(iii) Cluster-cored dendrimers could be prepared including ferrocenyl dendrimers, and the number of redox-active units has been successfully determined therein using the Bard–Anson equation in cyclic voltammetry. The pyridine-substituted clusters with small pyridine substituents are thermally stable, but the cluster-cored polyferrocenyl dendrimers have a limited thermal stability, probably because the large sizes of the dendrons destabilize the cluster–pyridine bond.

**Experimental Section**

**General Data.** Reagent-grade THF and pentane were predried over Na foil and distilled from a sodium benzophenone anion under argon immediately prior to use. Other commercial chemicals were purchased from Aldrich and used as received. All manipulations were carried out using Schlenk flasks, and samples were transferred in a nitrogen-filled, vacuum atmosphere drylab. $^1$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 Fourier transform mode at 75 MHz with a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per million ($\delta$, ppm) with reference to TMS. Elemental analyses were carried out at the Vernaison CNRS center. The infrared spectra were recorded in KBr pellets on a FT-IR Paragon 1000 Perkin-Elmer spectrometer.

**(i) MALDI-TOF Mass Spectrometry.** The MALDI mass spectra were recorded with a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated at an accelerating potential of 20 kV in both linear and reflection modes. The mass spectra shown represent an average of over 256 consecutive laser shots (3-Hz repetition rate). Peptides were used to calibrate the mass scale using the two-point calibration software 3.07.1 from PerSeptive Biosystems. Mentioned $m/z$ values correspond to monoisotopic masses. The solutions ($10^{-3}$ M) were prepared in THF. Matrix compounds were from Sigma (France) and used

without further purification. The matrixes, 2,5-dihydroxybenzoic acid (2,5-DHB), 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol), 6-azathiothymine, 2,4,6-trihydroxyacetophenone, 7-hydroxycoumarin, or 2-anthramine, were also dissolved in THF (10 g L$^{-1}$). A total of 1 $\mu$L of solution was mixed with 50 $\mu$L of the matrix solution. A total of 10 $\mu$L of an alkali iodide (LiI, NaI) solution (5 g L$^{-1}$ in THF) was added in some experiments to induce cationization. A total of 1 $\mu$L of the final solution was deposited onto the sample stage and allowed to dry in air.

Cyclic voltammetry data were recorded with a PAR 273 potentiostat galvanostat. The reference electrode was an Ag quasi-reference electrode (QRE). The QRE potential was calibrated by adding the reference couple [FeCp$_2$*]$^+$/[FeCp$_2$*] (Cp* = pentamethylcyclopentadienyl). The working electrode (platinum) was treated by immersion in 0.1 M HNO$_3$ and then polished before use and between each recording when necessary. The cluster [*n*-Bu$_4$N]$_2$[Mo$_6$Br$_8$(CF$_3$SO$_3$)$_6$] is irreversibly oxidized at +1.5 V vs Cp*$_2$Fe$^{+/0}$ in CH$_3$CN, whereas the hexa-*tert*-butylpyridine cluster **7** is irreversibly reduced at −0.7 V vs Cp*$_2$Fe$^{+/0}$ in dimethylformamide (DMF; both measurements were carried out at 25 °C, 0.2 V s$^{-1}$ with 0.1 M *n*-Bu$_4$NPF$_6$).

The syntheses and characterizations of the starting halogen cluster compounds M$_2$Mo$_6$X$_{14}$ have been performed according to the procedure described in ref 6e, and the synthesis of the triflate cluster compounds is reported in Shriver's publication.[12]

**Cluster Mo$_6$Br$_8$Py$_6$Tf$_4$, 5.** A yellow THF solution of **1** (0.585 g, 0.231 mmol) and pyridine (1.8 mL, 0.023 mol) was stirred at 60 °C for 2 days. The reaction product progressively precipitated from the reaction mixture as a very fine powder. The solvent was removed under vacuum to give an orange solid, which was washed with pentane and THF and dried under vacuum to yield complex **5** as an orange solid. Yield: 0.416 g of **5** (79%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.76 (d, 12H), 8.03 (m, 6H), 7.60 (m, 12H). $^{13}$C NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 147.7 (C$_o$), 141.5 (C$_p$), 126.3 (C$_m$). Elem anal. Calcd for C$_{34}$H$_{30}$Br$_8$F$_{12}$Mo$_6$N$_6$O$_{12}$S$_4$: C, 17.87; H, 1.32. Found: C, 17.21; H, 1.09. $M$ = 2285.76 g mol$^{-1}$.

**Cluster Mo$_6$I$_8$Py$_6$Tf$_4$, 6.** A yellow THF solution of **2** (0.686 g, 0.231 mmol) and pyridine (1.8 mL, 0.023 mol) was stirred at 60 °C for 2 days. The reaction product progressively precipitated from the reaction mixture as a very fine powder. The solvent was removed under vacuum to give an orange solid, which was washed with pentane and THF and dried under vacuum to yield complex **6** as an orange solid. Yield: 0.467 g of **6** (76%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.70 (d, 12H), 7.81 (m, 6H), 7.42 (m, 12H). $^{13}$C NMR (CD$_3$COCD$_3$, 75.47 MHz) $\delta_{ppm}$: 147.9 (C$_o$), 143.2 (C$_p$), 128.6 (C$_m$). Elem anal. Calcd for C$_{34}$H$_{30}$F$_{12}$I$_8$Mo$_6$N$_6$O$_{12}$S$_4$: C, 15.34; H, 1.14. Found: C, 14.69; H, 0.86. $M$ = 2661.77 g mol$^{-1}$.

**Cluster Mo$_6$Br$_8$(4-*tert*-butylpyridine)$_6$Tf$_4$, 7.** A THF solution of **1** (1 g, 0.394 mmol) and 4-*tert*-butylpyridine (2 mL) was stirred at 60 °C for 2 days. The solvent was removed under vacuum, and the product was precipitated with THF/pentane and dried under vacuum to yield complex **7** as an orange solid. Yield: 0.826 g (80%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.59 (d, 12H), 7.49 (d, 12H), 1.35 (s, 54H). $^{13}$C NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 147.4 (C$_o$), 122.1 (C$_m$), 34.5 (*C*Me$_3$), 30.7 (CH$_3$). Elem anal. Calcd for C$_{58}$H$_{78}$Br$_8$F$_{12}$Mo$_6$N$_6$O$_{12}$S$_4$: C, 26.56; H, 3.00. Found: C, 26.15; H, 2.69. $M$ = 2622.40 g mol$^{-1}$.

**Cluster Mo$_6$Br$_8$(4-vinylpyridine)$_6$Tf$_4$, 8.** A THF solution of **1** (0.300 g, 0.141 mmol) and 4-vinylpyridine (1 mL) was stirred at 60 °C for 2 days. The solvent was removed under vacuum to give a solid residue, which was washed with pentane and THF and dried under vacuum to yield complex **8** as an orange solid. Yield: 0.293 g (85%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.57 (d, 12H), 7.27

(d, 12H), 6.65 (q, 6H), 6.00 (d, 6H), 5.51 (d, 6H). $^{13}$C NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 150.5 (C$_o$), 135.1 (*C*H=CH$_2$), 121.1 (C$_m$), 119.0 (CH=*C*H$_2$). Elem anal. Calcd for C$_{46}$H$_{48}$Br$_8$F$_{12}$Mo$_6$N$_6$O$_{12}$S$_4$: C, 22.57; H, 1.98. Found: C, 22.09; H, 1.61. $M$ = 2448.04 g mol$^{-1}$.

**Cluster Mo$_6$I$_8$(4-*tert*-butylpyridine)$_6$Tf$_4$, 9.** A yellow THF solution of **2** (0.686 g, 0.231 mmol) and 4-*tert*-butylpyridine (1.8 mL) was stirred at 60 °C for 2 days. The solvent was removed under vacuum, and the product was precipitated with THF/pentane and dried under vacuum to yield complex **9** as an orange solid. Yield: 0.512 g of **9** (74%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.52 (d, 12H), 7.33 (m, 12H), 1.32 (m, 54H). $^{13}$C NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 147.4 (C$_o$), 122.1 (C$_m$), 34.5 (*C*Me$_3$), 30.7 (CH$_3$). Elem anal. Calcd for C$_{58}$H$_{78}$F$_{12}$I$_8$Mo$_6$N$_6$O$_{12}$S$_4$: C, 23.23; H, 2.62. Found: C, 22.52; H, 2.01. $M$ = 2998.41 g mol$^{-1}$.

**Cluster Mo$_6$I$_8$(4-vinylpyridine)$_6$Tf$_4$, 10.** A yellow THF solution of **2** (0.686 g, 0.231 mmol) and 4-vinylpyridine (1.8 mL) was stirred at 60 °C for 2 days. The reaction product progressively precipitated from the reaction mixture as a very fine powder. The solvent was removed under vacuum to give an orange solid, which was washed with pentane and THF and dried under vacuum to yield complex **10** as an orange solid. Yield: 0.528 g of **10** (81%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.46 (d, 12H), 7.17 (m, 12H), 6.52 (q, 6H), 5.85 (d, 6H), 5.38 (d, 6H). $^{13}$C NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 151.6 (C$_o$), 134.9 (*C*HCH$_2$), 122.3 (C$_m$), 120.0 (CH$_2$). Elem anal. Calcd for C$_{46}$H$_{48}$F$_{12}$I$_8$Mo$_6$N$_6$O$_{12}$S$_4$: C, 19.56; H, 1.71. Found: C, 19.37; H, 1.52. $M$ = 2824.04 g mol$^{-1}$.

**[RuCp(PPh$_3$)$_2$(CC−C$_5$H$_4$N)], 11.** A methanol solution of 4-ethynylpyridine (0.296 g, 2.07 mmol) and triethylamine (5 mL) was added to a suspension of [RuCp(PPh$_3$)$_2$Cl] (1 g, 1.38 mmol) and NH$_4$PF$_6$ (0.449 g, 2.76 mmol) in methanol. The solution was stirred at room temperature for 3 days. The solvent was removed under vacuum, and the product was extracted with toluene. The product was precipitated with toluene/pentane. The yellow powder was dried under vacuum. Yield: 0.350 g of **11** (32%). $^1$H NMR (MeOD, 300 MHz) $\delta_{ppm}$: 8.06 (d, NCH), 7.30−7.04 (m, PPh$_3$), 6.80 (d, NCCH), 4.29 (s, Cp). $^{31}$P NMR (MeOD, 100 MHz) $\delta_{ppm}$: 49.60 (PPh$_3$). IR: $\nu_{CC}$ 2070 cm$^{-1}$. MS (MALDI-TOF; *m/z*). Calcd for C$_{48}$H$_{39}$NP$_2$Ru: 792.85. Found: 794.24. CV in CH$_2$Cl$_2$: $E_{1/2}$ = 0.700 V vs Fc* at 20 °C (partially chemically reversible: $i_c/i_a$ = 0.5).

**Hexasubstituted Mo$_6$Ru$_6$ Cluster, 13.** A THF solution of **11** (0.131 g, 0.165 mmol) and **1** (0.069 g, 0.0265 mmol) was stirred at 60 °C for 7 days. The solvent was removed under vacuum, and the product was precipitated with THF/pentane. The red powder was dried under vacuum. Yield: 0.115 g of **13** (65%). Elem anal. Calcd for Mo$_6$Br$_8$C$_{292}$H$_{234}$F$_{12}$S$_4$O$_{12}$N$_6$P$_{12}$Ru$_6$: C, 53.39; H, 3.39. Found: C, 52.59; H, 2.97.

$^1$H NMR (MeOD, 300 MHz) $\delta_{ppm}$: 8.12 (d, NCH), 7.23−7.08 (m, PPh$_3$), 7.04 (d, NCCH), 4.42 (s, Cp). $^{31}$P NMR (MeOD, 100 MHz) $\delta_{ppm}$: 49.51 (PPh$_3$). IR: $\nu_{CC}$ 2018 cm$^{-1}$. CV in CH$_2$Cl$_2$: $E_{1/2}$ = 0.650 V vs Fc* at 20 °C in CH$_2$Cl$_2$ (partially chemically reversible: $i_c/i_a$ = 0.1).

**Hexaferrocenyl Mo$_6$Fc$_6$ Cluster, 14.** A THF solution of **12** (0.054 g, 0.187 mmol) and **1** (0.063 g, 0.029 mmol) was stirred at 60 °C for 7 days. The solvent was removed under vacuum, and the product was precipitated with THF/pentane. The red powder was dried under vacuum. Yield: 0.073 g of **14** (63%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.64 (d, NCH), 7.51 (d, NCCH), 4.62 and 4.41 (t, FeCH), 4.32 (s, Cp). $^{13}$C NMR (CDCl$_3$, 63 MHz) $\delta_{ppm}$: 69.9 (FeC), 70.2 (Cp), 72.0 (FeC), 76.95 (C), 125.9 (NC*C*), 147.5 (NC). IR: $\nu_{CC}$ 2 181 cm$^{-1}$. Elem anal. Calcd: C, 36.03; H, 2.22. Found: C, 35.29; H, 1.59. CV in CH$_2$Cl$_2$ at 20 °C: $E_{1/2}$ = 0.800 V vs [FeCp*$_2$] in CH$_2$Cl$_2$.

**Dendronic Pyridine Derivative, 15.** In a Schlenk tube, 3,5-bis-(bromomethyl)pyridine (0,17 mmol),[23] *p*-(triallylmethyl)phenol (1.13 mmol), and $K_2CO_3$ (2.26 mmol) were stirred for 2 days in acetonitrile. Then, the solvent was removed under vacuum, and the reaction product was extracted using diethyl ether and filtered on Celite. The solvent was evaporated to dryness, and the product **15** was chromatographed on silica gel (eluent: diethyl ether/petroleum ether, 1:1). Yield: 70%. $^1H$ NMR (250 MHz, CDCl$_3$) $\delta_{ppm}$: 8.66 (s, 2H, *o*-H pyridine), 7.90 (s, 1H, *p*-H pyridine), 7.23 and 6.96 (d, 4H, H aromatic), 5.55 (m, 6H, CH allyl), 5.02 (m, 12H, CH$_2$ allyl), 4.98 (s, 4H, CH$_2$O), 2.42 (d,12H, $C_q$−CH$_2$−CH). $^{13}C$ NMR (63 MHz, CDCl$_3$) $\delta_{ppm}$: 156.2 (C$_q$ Ar−O), 148.5−138.5 (CH pyridine), 134.53 (CH allyl), 132.6 (C$_q$ pyridine), 128.6−114.1 (CH Ar), 117.5 (CH$_2$ allyl), 67.3 (CH$_2$O), 44.7 (C$_q$ Ar−$C_q$−CH$_2$), 41.8 (C$_q$−CH$_2$−CH). Elem anal. Calcd for C$_{39}$H$_{45}$NO$_2$: C, 83.68; H, 8.10. Found: C, 83.23; H, 8.12. $M = 559.79$ g mol$^{-1}$.

**Dendronic Pyridine Derivative, 16.** In a Schlenk tube, 3,5-bis-(bromomethyl)pyridine (0.138 mmol), *p*-triferrocenylphenol[20] (0.415 mmol), and K$_2$CO$_3$ (0.83 mmol) were stirred for 2 days in acetonitrile at 40 °C. Then, the solvent was removed under vacuum, and the reaction product was extracted using diethyl ether and filtered on Celite. The solvent was evaporated to dryness, and the product was chromatographed on silica gel (eluent: diethyl ether/petroleum ether, 1:1). Yield: 44%. $^1H$ NMR (250 MHz, CDCl$_3$) $\delta_{ppm}$: 8.67 (s, 2H, *o*-H pyridine), 7.91 (s, 1H, *p*-H pyridine), 7.22 and 6.93 (d, 4H, H aromatic), 5.06 (s, 4H, CH$_2$O), 4.30−4.08−4.01 (CH ferrocenyl), 1.59−1.17 (m, 12H, C$_q$−CH$_2$−CH$_2$−CH), 0.64 (m, 6H, CH$_2$−Si), 0.16 (CH$_3$). $^{13}C$ NMR (63 MHz, CDCl$_3$) $\delta_{ppm}$: 155.8 (C$_q$ Ar−O), 148.5−132.7 (CH pyridine), 140.8 (C$_{qar}$−C$_q$), 134.6 (C$_q$ pyridine), 127.6−114.0 (CH$_{ar}$), 72.9−70.5−68.0 (CH ferrocenyl), 71.3 (C$_q$ ferrocenyl), 67.3 (CH$_2$O), 43.2 (C$_{qar}$−C$_q$−CH$_2$), 42.0 (C$_q$−CH$_2$−CH$_2$), 18.0 (CH$_2$−CH$_2$−CH$_2$), 17.5 (Si−CH$_2$), −1.9 (CH$_3$). Elem. anal. Calcd: C, 65.84; H, 7.02. Found: C, 66.71; H, 6.80.

**Hexasubstituted Cluster [Mo$_6$Br$_8$(dendron)$_6$][CF$_3$SO$_3$]$_4$, 17.** A yellow THF solution of **1** (0.100 g, 0.038 mmol) and the pyridine dendron **15** (0.143 g, 0.255 mmol) was stirred at 60 °C for 7 days. The solvent was removed under vacuum, and the product was precipitated with THF/pentane. The orange powder was dried under vacuum. Yield: 0.097 g of **17** (49%). $^1H$ NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.90 (s, 12H, H$_o$), 8.66 (s, 6H, H$_p$), 7.27 (d, 24H), 6.96 (d, 24H), 5.53 (m, 36H, =CH$_a$), 5.02 (m, 96H, =CH$_{2a}$ + OCH$_2$), 2.45 (d, 72H, CH$_2$). $^{13}C$ NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 155.46 (C$_o$), 139.19 (C$_m$), 136.91 (C$_p$), 134.26 (CH=CH$_2$), 127.96 (C$_{ar}$), 117.41 (CH=CH$_2$), 114.20 (C$_{ar}$), 65.95 (OCH$_2$), 42.84 (C$_q$), 41.85 (C$_q$−CH$_2$). Elem anal. Calcd for C$_{238}$H$_{270}$Br$_8$F$_{12}$Mo$_6$N$_6$O$_{24}$S$_4$: C, 55.29; H, 5.26. Found: C, 54.85; H, 4.98. $M = 5169.83$ g mol$^{-1}$.

**Hexasubstituted Cluster [Mo$_6$Br$_8$(dendron)$_6$][CF$_3$SO$_3$]$_4$, 18.** A yellow THF solution of **1** (0.012 g, 0.0046 mmol) and ′**12** (0.058 g, 0.0285 mmol) was stirred at 60 °C for 6 days. The solvent was removed under vacuum, and the product was precipitated with CH$_2$Cl$_2$/pentane to give an orange solid **18**. Yield: 0.039 g of **18** (59%). $^1H$ NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.82 (m, 12H), 8.50 (m, 6H), 7.22 (d, 24H), 6.92 (d, 24H), 5.20 (s, 24H), 4.31 (s, 72H), 4.08 (s, 180H), 4.02 (s, 72H), 1.63 (m, 72H), 1.12 (m, 72H), 0.64 (m, 72H), 0.16 (s, 216H). $^{13}C$ NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 141.7 (C$_{ar}$), 127.7 (C$_{ar}$), 113.9 (C$_{ar}$), 72.9 (C$_{ar}$), 71.0 (OCH$_2$), 70.6 (C$_{ar}$), 68.1 (Cp), 43.3 (C$_q$−CH$_2$), 18.0 (CH$_2$), 17.4 (SiCH$_2$), −2.0 (SiCH$_3$). Elem. anal. Calcd for C$_{670}$H$_{846}$Br$_8$F$_{12}$Fe$_{36}$Mo$_6$N$_6$O$_{24}$S$_4$Si$_{36}$: C, 57.64; H, 6.11. Found: C, 55.97; H, 5.22. $M = 13\,960.80$ g mol$^{-1}$.

**Cluster [Mo$_6$Br$_{13}$(4-*tert*-butylpyridine)][*n*-Bu$_4$N], 20.** A THF solution of [*n*-Bu$_4$N]$_2$[Mo$_6$Br$_{13}$(CF$_3$SO$_3$)], **19** (0.426 g, 0.19 mmol), and 4-*tert*-butylpyridine (0.028 mL, 0.19 mmol) was stirred at 60 °C for 2 days. The solvent was removed under vacuum to give an orange solid, which was washed with pentane and THF and dried under vacuum to yield complex **20** as an orange solid. Yield: 0.181 g (48%). $^1H$ NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.57 (d, 2H), 7.36 (d, 2H), 1.34 (s, 9H). $^{13}C$ NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 146.8 (C$_o$), 122.2 (C$_m$), 33.9 (CMe$_3$), 30.1 (CH$_3$). Elem anal. Calcd for C$_{25}$H$_{49}$-Br$_{13}$Mo$_6$N$_2$: C, 15.07; H, 2.48. Found: C, 14.68; H, 2.27. $M = 1992.07$ g mol$^{-1}$.

**Cluster [Mo$_6$Br$_{13}$(4-vinylpyridine)][*n*-Bu$_4$N], 21.** A THF solution of **19** (0.426 g, 0.19 mmol) and 4-vinylpyridine (0.021 mL, 0.19 mmol) was stirred at 60 °C for 2 days. The solvent was removed under vacuum to give an orange solid, which was washed with pentane and THF and dried under vacuum to yield complex **20** as an orange solid. Yield: 0.138 g (37%). $^1H$ NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.54 (d, 2H), 7.26 (d, 2H), 6.61 (q, 1H), 5.93 (d, 1H), 5.46 (d, 1H). $^{13}C$ NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 150.5 (C$_o$), 135.1 (CHCH$_2$), 121.1 (C$_m$), 119.0 (CH$_2$). Elem anal. Calcd for C$_{23}$H$_{43}$Br$_{13}$Mo$_6$N$_2$: C, 14.08; H, 2.21. Found: C, 13.73; H, 2.02. $M = 1962.00$ g mol$^{-1}$.

**Pyridine Dendron 22.** In a Schlenk tube, 3,5-bromomethyl-pyridine (1.5 mmol), dimethyl 5-hydroxyisophthalate (6 mmol), and K$_2$CO$_3$ (12 mmol) were stirred for 1 day in acetonitrile at 60 °C. Then, the solvent was removed under vacuum, and the reaction product was extracted using diethyl ether and filtered on Celite. The solvent was evaporated to dryness, and the product was chromatographed on silica gel (eluent: diethyl ether/petroleum ether, 1:1). Yield: 60%. $^1H$ NMR (250 MHz, CDCl$_3$) $\delta$: 8.70 (s, 2H), 7.94 (s, 1H), 8.34 (s, 2H), 7.85 (s, 4H), 5.21 (s, 4H), 3.95 (s, 12H). $^{13}C$ NMR (63 MHz, CDCl$_3$) $\delta_{ppm}$: 165.8 (C$_q$), 158.3 (C$_q$−O), 148.6−134.5 (CH), 132.7 (C$_q$−C$_q$OO), 123.7 (*p*-CH$_{ar}$), 120.0 (*o*-CH$_{ar}$), 67.7 (CH$_2$−O), 52.4 (CH$_3$). Elem anal. Calcd: C, 61.95; H, 4.81. Found: C, 61.75; H, 4.96.

**Pyridine Dendron 23.** To a suspension of LiAlH$_4$ (19.8 mmol) in dry THF was added the pyridine dendron **22** (1.98 mmol) dissolved in the same solvent. After 6 h of reflux, 4 mL of water was slowly added in an ice bath. Then, the product was filtered and extracted with hot methanol. A yellow solid was obtained after precipitation with diethyl ether. Yield: 71%. $^1H$ NMR (250 MHz, methanol-$d_4$) $\delta$: 8.59 (s, 2H), 8.03 (s, 1H), 6.95 (s, 6H), 5.19 (s, 4H), 4.57 (s, 8H). $^{13}C$ NMR (63 MHz, CD$_3$OD) $\delta_{ppm}$: 158.7 (C$_q$−O), 147.2−135.1 (CH), 133.8 (C$_q$), 143.2 (C$_{qar}$), 117.7 (*p*-CH$_{ar}$), 111.6 (*o*-CH$_{ar}$), 66.7 (CH$_2$−O), 63.5 (CH$_2$OH).

**Pyridine Dendron 24.** In a Schlenk tube, the pyridine dendron **23** (0.79 mmol) was stirred at 0 °C during the addition of tribromophosphine (1.05 mmol). After 4 h in DMF at room temperature, the product was extracted with dichloromethane; this solution was washed several times with water and dried over Na$_2$SO$_4$, and the solent was removed under vacuum, yielding a white solid. Yield: 44%. $^1H$ NMR (250 MHz, CDCl$_3$) $\delta$: 8.67 (s, 2H), 7.90 (s, 1H), 7.05 (s, 2H), 6.95 (s, 4H), 5.13 (s, 4H), 4.44 (s, 8H). $^{13}C$ NMR (63 MHz, CDCl$_3$) $\delta_{ppm}$: 158.6 (C$_q$−O), 148.0−134.9 (CH), 132.3 (C$_q$), 139.8 (C$_{qar}$−CH$_2$Br), 122.5 (*p*-CH$_{ar}$), 115.4 (*o*-CH$_{ar}$), 67.3 (CH$_2$−O), 32.6 (CH$_2$Br). Elem anal. Calcd: C, 41.66; H, 3.19. Found: C, 41.57; H, 3.34.

**12-Ferrocenylpyridine Dendron, 25.** In a Schlenk tube, pyridine **24** (0,0052 mmol), *p*-triferrocenylphenol[20] (0.029 mmol), and K$_2$CO$_3$ (0.063 mmol) were stirred for 2 days in acetonitrile at room temperature. Then, the solvent was removed under vacuum, and the reaction product was extracted using diethyl ether and filtered on Celite. The solvent was evaporated to dryness, and the product was chromatographed on silica gel (eluent: diethyl ether/petroleum ether, 7:3). Yield: 22%. $^1H$ NMR (250 MHz, CDCl$_3$)

$\delta_{ppm}$: 8.68 (s, 2H, $o$-H pyridine), 7.90 (s, 1H, $p$-H pyridine), 7.26 and 6.90 (d, 16H, H aromatic), 6.97 (s, 4H, $o$-CH$_{ar}$), 6.93 (s 2H, $p$-CH$_{ar}$), 5,12 (s, 4H, CH$_2$O), 5,02 (s, 8H, CH$_2$O), 4.30–4.08–4.01 (CH ferrocene), 1.59–1.17 (m, 12H, C$_q$–CH$_2$–CH$_2$–CH), 0.64 (m, 6H, CH$_2$–Si), 0.16 (CH$_3$). $^{13}$C NMR (63 MHz, CDCl$_3$) $\delta_{ppm}$: 127.6–114.0 (CH$_{ar}$), 72.9–70.5–68.0 (CH ferrocenyl), 71.3 (C$_q$ ferrocenyl), 67.3 (CH$_2$O), 43.6 (C$_{qar}$–C$_q$–CH$_2$), 42.4 (C$_q$–CH$_2$–CH$_2$), 18.4 (CH$_2$–CH$_2$–CH$_2$), 17.9 (Si–CH$_2$), −1.53 (CH$_3$). Elem anal. Calcd: C, 66.13; H, 7.23. Found: C, 65.80; H, 6.66.

**Ferrocenyl-Dendronized Cluster, 26.** A yellow THF solution of **19** (0.016 g, 0.007 mmol) and ′**25** (0.032 g, 0.007 mol) was stirred at 60 °C for 2 days. The solvent was removed under vacuum to give an orange solid. Yield: 0.042 g of **26** (35%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$: 8.79 (m, 2H), 8.22 (m, 1H), 7.21 (d, 12H), 7.19 (m, 2H), 6.95 (d, 8H), 5.19 (s, 4H), 5.04 (s, 8H), 4.32 (s, 24H), 4.10 (s, 60H), 4.04 (s, 24H), 3.75 (t, 8H), 1.87 (m, 8H), 1.62 (m, 32H), 1.11 (m, 24H), 0.6 (m, 24H), 0.15 (s, 72H). $^{13}$C NMR (CDCl$_3$, 75.47 MHz) $\delta_{ppm}$: 129.5–116.0 (CH$_{ar}$), 74.9– 73.3–70.0 (CH ferrocenyl), 72.6 (C$_q$ ferrocenyl), 45.2 (C$_{qar}$–$C_q$–CH$_2$), 44.0 (C$_q$–$C$H$_2$–CH$_2$), 20.0 (CH$_2$), 19.46 (Si–CH$_2$), 2.9 (CH$_3$).

**Supporting Information Available:** Structures and $^1$H NMR spectra for complexes **5**−**11**, **13**−**18**, **25**, and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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