Synthesis of Highly Charged Organometallic Dendrimers and Their Characterization by Electrospray Mass Spectrometry and Single-Crystal X-ray Diffraction

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Abstract: Four new carbosilane dendrimers terminated with 12, 24, 36, and 72 benzyl groups have been synthesized and characterized by matrix-assisted laser desorption/ionization−time-of-flight mass spectrometry. These dendrimers were capped with Cp^*Ru^+ to yield polycations containing charges of 12+, 24+, 36+, and 72+. The charged dendrimers comprise the largest such structures thus far characterized by electrospray ionization (ESI) mass spectrometry. Additionally, for the first time full resolution of individual isotopic distributions has been achieved using ESI FT-ICR techniques, thereby providing unambiguous confirmation of the charges and nuclearities of the dendrimers. The first-generation, ruthenium-containing dendrimer (**G1-Ru$_{12}$**) was also characterized by single-crystal X-ray diffraction. This polycation has a molecular volume significantly larger than any dendrimer thus far characterized by this technique.

There has been significant recent interest in the construction of well-defined structures from building blocks with nanometer-size dimensions, for potential applications in such areas as molecular recognition, shape selective catalysis, and self-assembly.[1] Examples of nanoscale building blocks that have been employed for construction of higher order materials include nanocrystallites,[2] amphiphilic liquid crystals,[3] and high-nuclearity metal clusters.[4] Another class of molecules with dimensions in the nanometer size regime are dendritic macromolecules. Recent research efforts have moved toward application of these novel polymers as photorefractive materials,[5] catalysts,[6] and liquid crystals.[7] However, there have been few reports on the use of dendrimers as nanoscale building blocks for higher order materials.[8]

Our interest in the synthesis of dendrimers comes from their potential use as nanoscopic building blocks for novel superlattice materials. In particular, we are interested in the construction of superlattice structures via combinations of charged, spherically shaped dendrimers possessing cationic or anionic end-groups. For this purpose we have embarked on synthetic investigations targeting dendrimers which can be obtained in large quantities, with well-defined shapes and functionalities. Although syntheses of dendritic polyanions with the requisite characteristics have been reported,[9] examples of the corresponding polycations are still quite rare.[9f,10] In our studies, we have also targeted metal-containing dendrimers which should be readily imaged by transmission electron microscopy (TEM).

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Quite recently, Aida and co-workers have demonstrated the electrostatic assembly of charged dendrimers into higher order topologies and have studied the resulting materials using flouresence polarization methods.[8i]

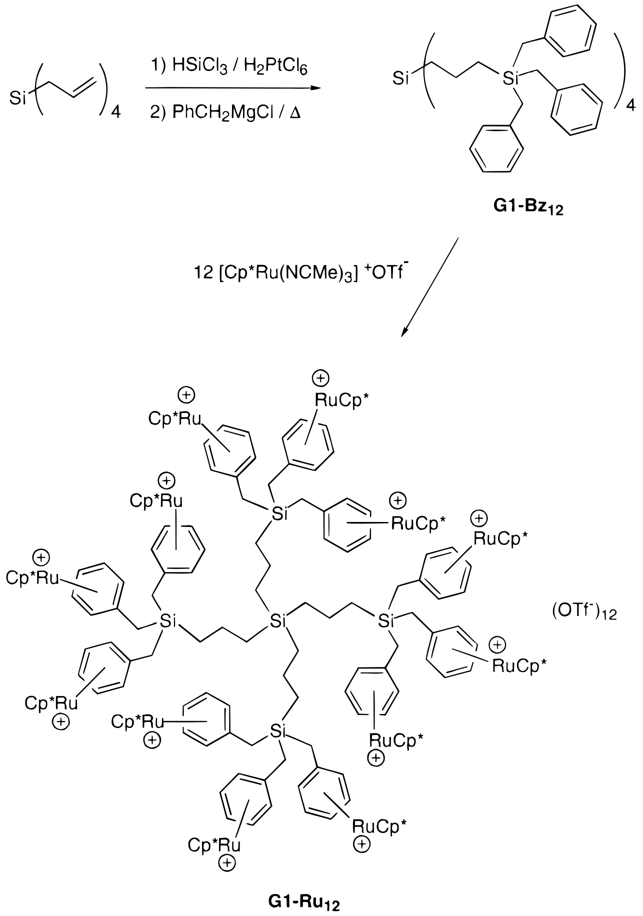
Herein we wish to report the isolation of several highly charged, polycationic dendrimers that have potential use as nanoscale building blocks. Since we wish to achieve a roughly spherical molecular shape, the divergent synthetic scheme for neutral carbosilane dendrimer cores has been employed.[11] Functionalization of the periphery of the dendrimers with robust cationic centers was accomplished with the reagent $[Cp^*Ru(NCMe)_3]^+OTf^-$ ($Cp^* = C_5Me_5$, $OTf = O_3SCF_3$), which is known to form stable cationic η^6-arene complexes with a variety of substrates containing aromatic groups.[12] We have synthesized first, second, and third generation organoruthenium dendrimers bearing charges of 12+, 24+, 36+, and 72+. The first generation dendrimer, **G1-Ru$_{12}$**, was characterized by single-crystal X-ray diffraction, and all cationic dendrimers reported in this paper were characterized by electrospray ionization (ESI) mass spectrometry. Significantly, full resolution of the individual isotopic distributions for each charged state in the ESI Fourier transform-ion cyclotron resonance (ESI FT-ICR) mass spectrum has been achieved, providing unambiguous and thorough characterization of these highly charged species.

Results and Discussion

The method employed for growth of the neutral dendrimers is based on the hydrosilation of allyl- or vinyl-terminated carbosilanes with a chlorosilane, followed by introduction of propagating or capping end groups with a Grignard reagent (Schemes 1, 2, and 3). This general synthetic procedure, pioneered by van der Maade,[11a] Seyferth,[11b] and Roovers,[11c] represents an efficient method for effecting the divergent growth of dendrimers from a tetrahedral core. Its success in producing high yields of monodisperse species depends markedly on the experimental conditions employed. In particular, we have found that chloroplatinic acid (CPA) is more effective than Karstedt's catalyst in achieving complete hydrosilations. In addition, cleaner silyl chloride dendrimers were more reliably obtained with CPA catalyst that had been stirred in dry 2-propanol, in the dark, for 48 h prior to use.[13] We also found that the use of freshly distilled chlorosilanes ($HSiCl_3$ or $HSiMeCl_2$) significantly shortened the required reaction times. Finally, the cleanest hydrosilations were achieved by rapidly heating the reaction mixture until an exotherm was observed (as seen by gentle refluxing of the reaction mixture) and then allowing the mixture to cool to room temperature before heating again for 3−10 h (see Experimental Section for further details).

The first-generation, benzyl-terminated dendrimer **G1-Bz$_{12}$** was synthesized by the hydrosilation of tetraallylsilane (**G0-Al$_4$**) with trichlorosilane,[11a] followed by addition of 12 equiv of benzyl Grignard (Scheme 1). After chromatographic purification, **G1-Bz$_{12}$** was isolated in 71% yield as a colorless oil that was characterized by matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry and NMR spectroscopy. The MALDI mass spectrum of **G1-Bz$_{12}$** contained a single molecular ion peak at 1426 Da, indicating that the sample was monodisperse.

Scheme 1



Cationic ruthenium centers were introduced by the reaction of **G1-Bz$_{12}$** with 12 equiv of $[Cp^*Ru(NCMe)_3]^+OTf^-$ in CH_2Cl_2 for 2 h at 45 °C, which gave **G1-Ru$_{12}$** in high yield (85%) as an off-white solid after precipitation from diethyl ether (Scheme 1). The ^1H and ^{13}C NMR spectra of this dendrimer exhibit the characteristic upfield shift for the aromatic resonances, indicating coordination of the Cp^*Ru^+ group. However, interpretation of the MALDI mass spectrum of **G1-Ru$_{12}$** was not straightforward. In addition to an $[M - OTf]^+$ peak, several unassignable low molecular weight peaks were also observed.

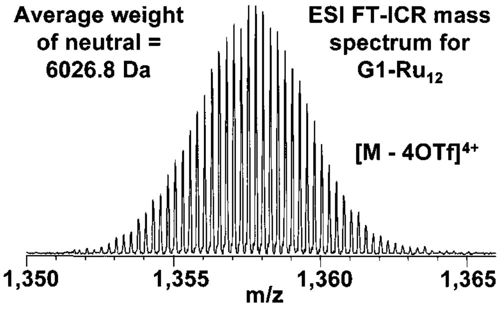


Figure 1. ESI FT-ICR $[M - 4OTf]^{4+}$ isotopic distribution for **G1-Ru$_{12}$** with composition $C_{224}H_{288}Si_5Ru_{12}S_8O_{24}F_{24}$.

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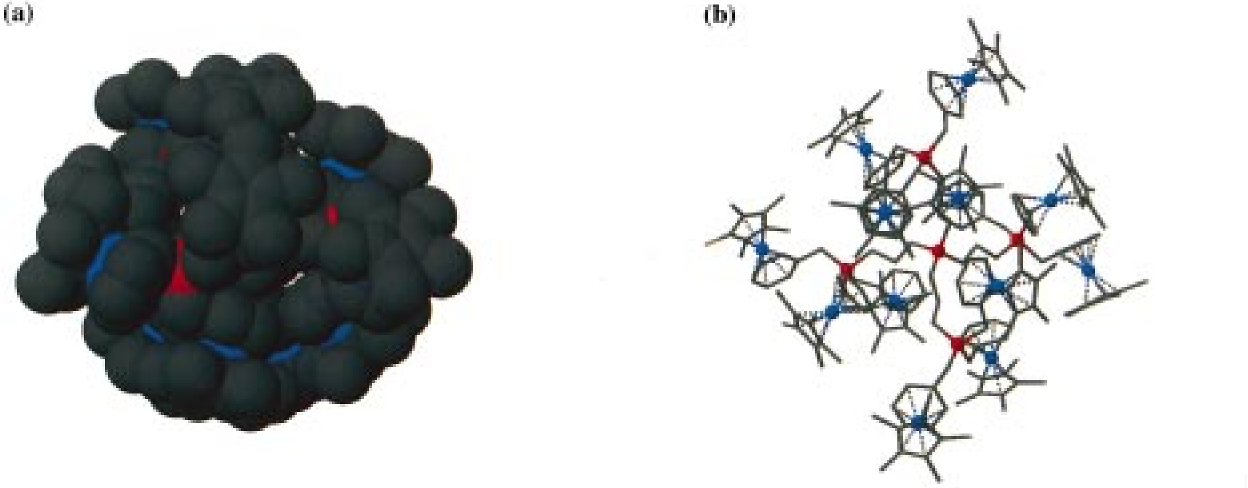

Figure 2. X-ray structure of **G1-Ru$_{12}$** represented as a space-filling (a) and ball-and-stick (b) model. The Ru atoms are shown in blue, the Si atoms in red, and the C atoms in gray. The triflates have been omitted for clarity.

More definitive mass spectra of **G1-Ru$_{12}$** were obtained by the electrospray mass spectrometry (ESI) technique, which revealed the 3+ and 4+ charged states as the only two peaks in the spectrum. At this time, it is unclear why no other charged states appeared in the ESI spectrum of **G1-Ru$_{12}$**. Unambiguous assignments of these charge states were provided by ESI FT-ICR mass spectrometry. The ESI FT-ICR spectrum of **G1-Ru$_{12}$** exhibited cleanly resolved isotopic distributions centered at *m*/*z* 1357.8 and 1860.4, corresponding to $[M - 4OTf]^{4+}$ (Figure 1) and $[M - 3OTf]^{3+}$, respectively.

Given our interest in dendrimers as building blocks in supramolecular chemistry, we have been motivated to determine the tertiary structures associated with various dendrimeric architectures. Indeed, very little is known about the solid state structures of dendrimers, and only a few have been characterized by single-crystal X-ray diffraction.[10f,11b,14] X-ray quality crystals of **G1-Ru$_{12}$** were obtained by slow vapor diffusion of Et_2O into a CH_2Cl_2 solution of the dendrimer. Views of the structure are provided in Figures 2a and 2b. **G1-Ru$_{12}$** crystallized in an orthorhombic unit cell of space group *Fdd*2. There are 16 dendrimers per unit cell with an overall cell volume of 105 761 Å^3 ($a = 53.805(1)$ Å; $b = 40.813(1)$ Å; $c = 48.161(1)$ Å). The 12 triflate anions are closely associated with the dendrimer dodecacations, with 9 of them residing within the periphery of the dendrimer. Despite the fact that there is some disorder in two triflates and an associated solvent molecule, the *R* value was a remarkable 7.89%.

The diameter of the cation was estimated from a space-filling model (Figure 2a) as 23−28 Å. The somewhat irregular (nonspherical) shape is not unexpected for this early generation. From the ball-and-stick model (Figure 2b), it can be seen that the dendrimer has an approximate C_2 axis passing through the central silicon atom. With representation of the dendrimers as 23 Å diameter spheres, the structure may be described as a fairly "open" body-centered cubic (bcc) lattice (Figure 3). To our knowledge, this is by far the largest dendrimer (in terms of molecular weight and molecular volume) to be characterized by single-crystal X-ray diffraction.

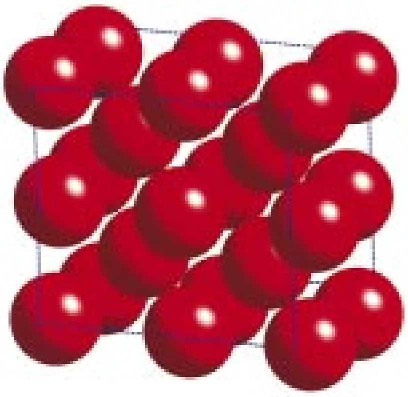

Figure 3. Diagram showing the bcc-type packing of the **G1-Ru$_{12}$** dendrimers, represented as idealized spheres with 23 Å diameters, and the unit cell for the structure.

The second-generation dendrimer **G2-Bz$_{36}$** was synthesized by hydrosilation of **G1-Al$_{12}$** with $HSiCl_3$,[11a] followed by the addition of 36 equiv of benzyl Grignard (Scheme 2). After chromatographic purification and repeated washings with hexanes, **G2-Bz$_{36}$** was isolated in 65% yield as a highly viscous colorless oil. Well-resolved, sharp peaks in the ^{1}H and ^{13}C NMR spectra are consistent with a monodisperse dendrimer sample. The MALDI-TOF mass spectrum of **G2-Bz$_{36}$** provided further support for this conclusion by virtue of a single peak corresponding to the quasimolecular ion at 4452 Da (M + Na).

Reaction of **G2-Bz$_{36}$** with $[Cp^*Ru(NCMe)_3]^+OTf^-$ in CH_2Cl_2 afforded an off-white powder, for which the ^{1}H NMR spectrum suggested that complete complexation of the aromatic groups had occurred to yield the desired **G2-Ru$_{36}$** dendrimer. However, the corresponding ESI data revealed that a mixture of dendrimers containing both 36 Cp^*Ru^+ and 35 Cp^*Ru^+ groups had been isolated. To further corroborate these data, a high-resolution ESI FT-ICR mass spectrum of these reaction products was obtained. The ESI FT-ICR spectrum showed clear isotopic resolution of the 8+ (Figure 4), 7+, 6+, and 5+ charged states for **G2-Ru$_{36}$** at 2136.0, 2465.8, 2902.0, and

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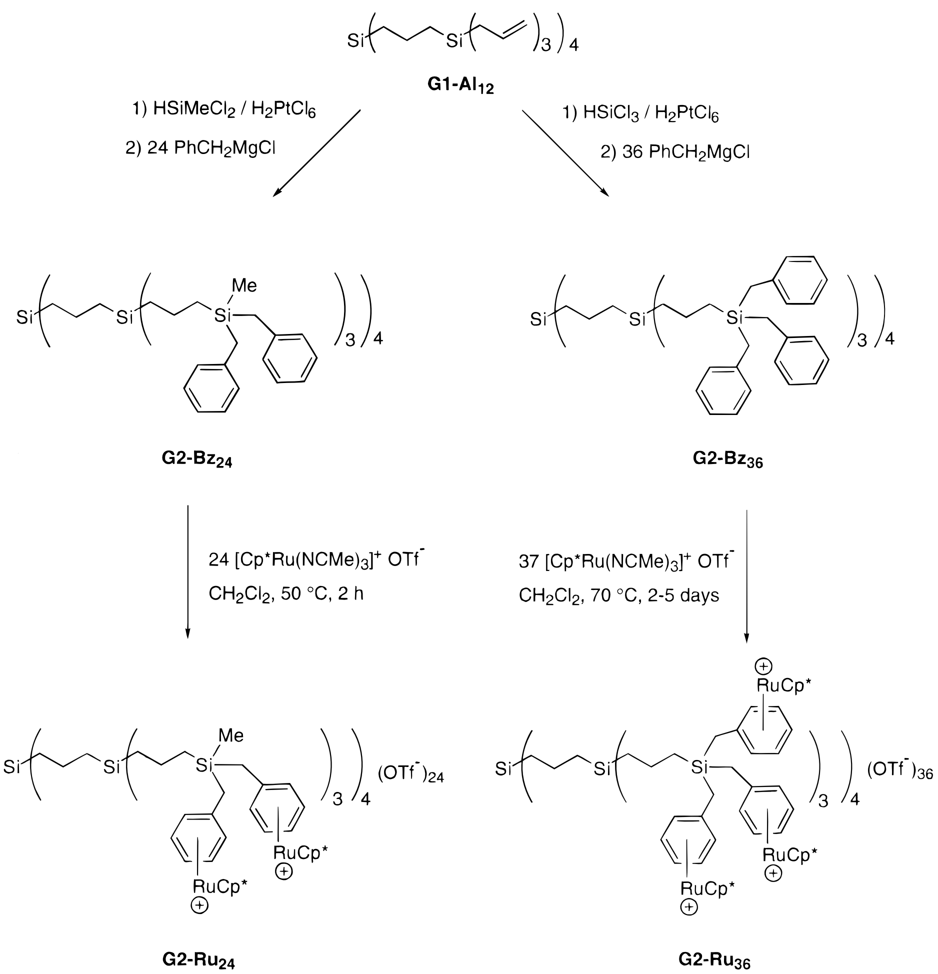
[14] See, for example: (a) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 4195. (b) Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1995**, *14*, 5362. (c) Lambert, J.; Pflug, J.; Stern, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98. (d) Lambert, J.; Pflug, J.; Denari, J. *Organometallics* **1996**, *15*, 615. (e) Nanjo, M.; Sekiguchi, A. *Organometallics* **1998**, *17*, 492. (f) Brewis, M.; Clarkson, G. J.; Goddard, V.; Helliwell, M.; Holder, A. M.; Mckeown, N. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1092.

Scheme 2



3512.4 Da, respectively. Additionally, the corresponding ions for the dendrimer with only 35 Cp*Ru$^+$ groups, **G2-Ru$_{35}$**, were also observed, albeit at much lower relative abundance. Even after prolonged reaction times (2−5 days) at elevated temperatures (70−90 °C) and numerous (20−30) vacuum evaporations of the solvent with subsequent redilution in CH$_2$Cl$_2$ (to remove acetonitrile), **G2-Ru$_{36}$** could not be isolated as the sole product. Presumably, steric congestion at the periphery of the dendrimer prevented complete complexation of all 36 terminal benzyl groups.

To test the above hypothesis, we synthesized the dendrimer **G2-Bz$_{24}$** (Scheme 2). Since this dendrimer is analogous to **G2-Bz$_{36}$** in generation number but has one less benzyl group at each terminal Si atom, we reasoned that addition of the Cp*Ru$^+$ moiety would be much more facile. This dendrimer was readily synthesized in 66% yield by hydrosilation of **G1-Al$_{12}$** with HSiMeCl$_2$, followed by addition of excess benzylmagnesium chloride. As in the case of **G2-Bz$_{36}$** the MALDI-TOF mass spectrum of **G2-Bz$_{24}$** exhibited a single peak with an *m*/*z* value corresponding to the molecular weight of the desired product.

Treatment of **G2-Bz$_{24}$** with 24 equiv of [Cp*Ru(NCMe)$_3$]$^+$-OTf$^-$ yielded **G2-Ru$_{24}$** in 83% yield. As expected, the ^{1}H and ^{13}C NMR spectra for **G2-Ru$_{24}$** exhibited an upfield shift for the aromatic resonances relative to those of **G2-Bz$_{24}$**. The low-resolution ESI mass spectrum contained ions for the 4+, 5+, 6+, and 7+ charged states, although the resolution was not sufficient to resolve the isotopic distributions for any of these species. Thus, FT-ICR was employed to corroborate the low-resolution ESI data and provide supporting evidence for the formation of these charged states. The ESI FT-ICR mass

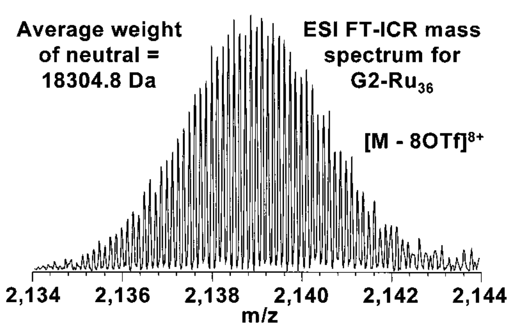


Figure 4. ESI FT-ICR [M − 8OTf]$^{8+}$ isotopic distribution for **G2-Ru$_{36}$** with composition $C_{664}H_{888}O_{84}Si_{17}Ru_{36}S_{28}F_{84}$.

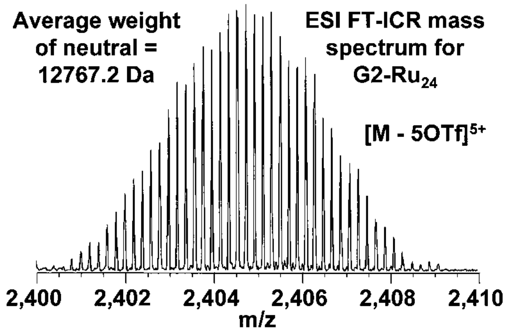
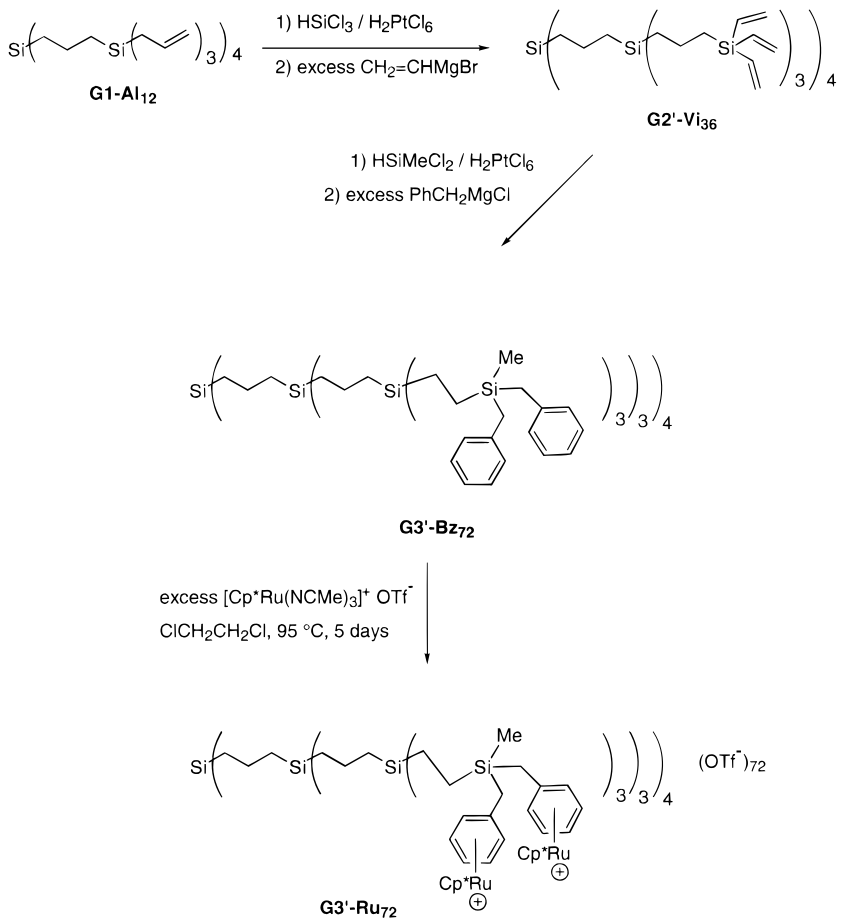


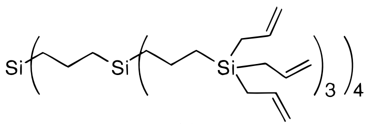
Figure 5. ESI FT-ICR [M − 5OTf]$^{5+}$ isotopic distribution for **G2-Ru$_{24}$** with composition $C_{487}H_{660}O_{57}Si_{17}Ru_{24}S_{19}F_{57}$.

Scheme 3



spectrum (Figure 5) revealed these same charged states with complete resolution of the isotopic distributions and no evidence for the presence of dendrimers containing fewer than 24 ruthenium atoms. In addition, these spectra match the simulated isotopic envelopes for each of the observed charged states and thus provide unequivocal characterization of the nuclearity of **G2-Ru$_{24}$**.

An attempt to synthesize a dendrimer with 72 benzyl end groups was based on hydrosilation of the known compound **G2-Al$_{36}$**[11a] with $HSiMeCl_2$. However, this hydrosilation could not be driven to completion. Since vinyl silanes are more active than allyl silanes toward hydrosilation,[15] a related approach was based on **G2′-Vi$_{36}$**, which was synthesized in 48% yield by means of hydrosilation of **G1-Al$_{12}$** with $HSiCl_3$ and subsequent reaction with vinylmagnesium bromide (Scheme 3). The ^{1}H and ^{13}C NMR and MALDI-TOF spectra of **G2′-Vi$_{36}$** indicated that this dendrimer had formed cleanly to give a monodisperse sample.



G2-Al$_{36}$

Since it has been well established that hydrosilations of vinyl silanes are particularly prone to giving a mixture of regioisomers,[11b,15] the hydrosilation of **G2′-Vi$_{36}$** with $HSiMeCl_2$ was conducted in the presence of PPh_3, which was expected to promote formation of the β-derivatives $\sim SiCH_2CH_2SiMeCl_2$.[16] Indeed, this reaction proceeded smoothly over 5 h at 60 °C, and following addition of excess benzyl Grignard and subsequent chromatographic purification, **G3′-Bz$_{72}$** was isolated as a colorless glass in 56% yield. Spectroscopic characterization of this dendrimer by ^{1}H and ^{13}C NMR spectroscopy was more difficult than for the lower-generation dendrimers, due to extremely broad resonances in the spectra. This peak broadening suggests severe steric crowding within the dendrimer.[17] The MALDI-TOF mass spectrum of **G3′-Bz$_{72}$** revealed the presence of a predominant peak with a m/z value corresponding to the desired product, as well as several lower molecular weight peaks which are attributed to dendrimers derived from incomplete hydrosilation reactions. The observed imperfections present in the third generation are consistent with literature reports regarding divergent synthetic schemes, which tend to produce increasingly polydisperse dendrimers with each successive generation.[18]

The reaction of **G3′-Bz$_{72}$** with excess $[Cp^*Ru(NCMe)_3]^+OTf^-$ required forcing conditions to achieve complete complexation of the arenes. Thus, this reaction was carried out in 1,2-dichloroethane at 95 °C for 5 days; repeated removal of solvent under vacuum, followed by addition of fresh 1,2-dichloroethane, helped drive the reaction to completion. The 72+ cationic

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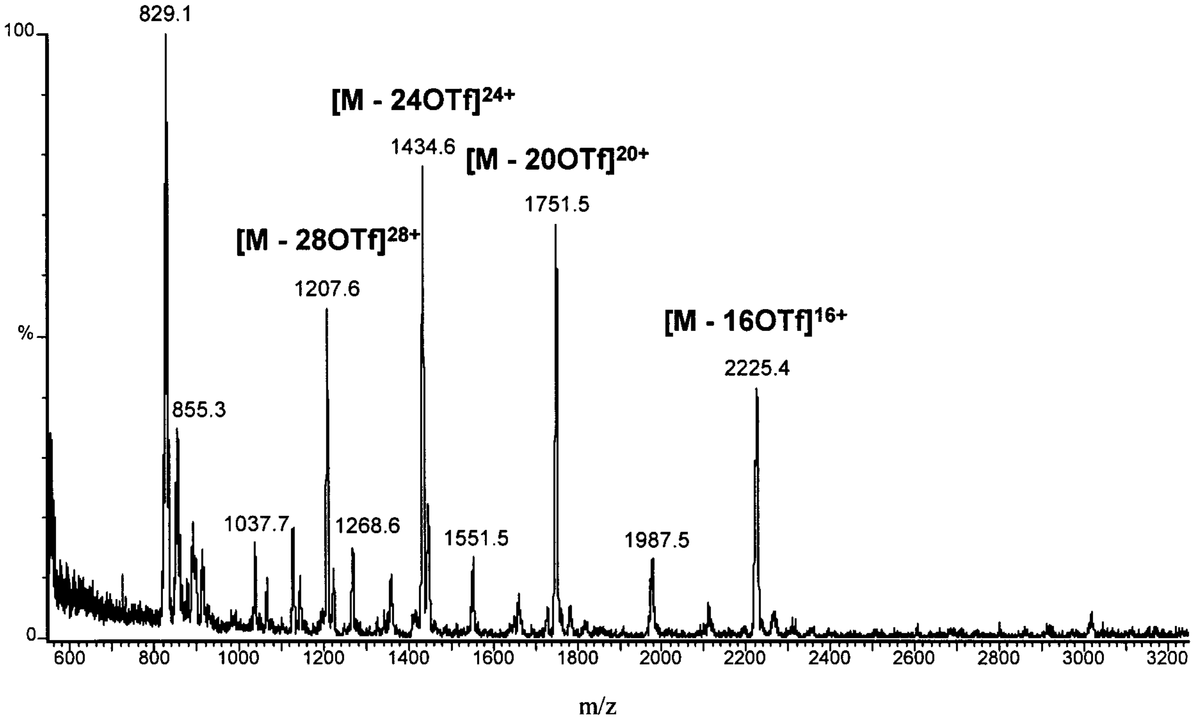
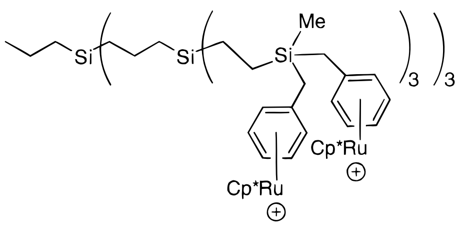


Figure 6. Low-resolution ESI mass spectrum for **G3′-Ru$_{72}$** with composition $C_{1436}H_{1944}O_{168}Si_{53}Ru_{72}S_{56}F_{168}$ ($[M - 16OTf]^{16+}$), $C_{1432}H_{1944}O_{156}Si_{53}Ru_{72}S_{52}F_{156}$ ($[M - 20OTf]^{20+}$), $C_{1428}H_{1944}O_{144}Si_{53}Ru_{72}S_{48}F_{144}$ ($[M - 24OTf]^{24+}$), $C_{1424}H_{1944}O_{132}Si_{53}Ru_{72}S_{44}F_{132}$ ($[M - 28OTf]^{28+}$).

dendrimer **G3′-Ru$_{72}$** was isolated in 77% yield by precipitation with Et_2O. Characterization of **G3′-Ru$_{72}$** by ^1H NMR spectroscopy was extremely difficult due to broad resonances in the spectrum. However, no aromatic peaks were visible in the region of 6.6−7.4 ppm, suggesting that complete arene complexation had occurred. The ESI spectrum of **G3′-Ru$_{72}$** revealed intense peaks corresponding to the 28+, 24+, 20+, and 16+ charged states (Figure 6). However, due to the high molecular weight of **G3′-Ru$_{72}$** (38,000 Da), peaks corresponding to incomplete Cp^*Ru^+ functionalization of **G3′-Bz$_{72}$** could potentially overlap with those assigned above. The ESI FT-ICR mass spectrum revealed only three extremely well resolved isotopic distributions, corresponding to a species with the charged states $[M - 5OTf]^{5+}$, $[M - 4OTf]^{4+}$, and $[M - 3OTf]^{3+}$. Surprisingly, these peaks correspond to a species with a molecular weight of approximately 9499 Da. The only reasonable species with this molecular weight corresponds to a fragment of **G3′-Ru$_{72}$** resulting from cleavage of a Si−C bond at the central silicon (**A**). We assume that this fragmentation occurs under the ionizing conditions of the ESI FT-ICR analysis, since such a process seems inconsistent with the relatively mild synthetic conditions.[19] Additionally, since the source design of the ESI FT-ICR instrument is such that ions are collected in an octapole trapping region during ion accumulation (which occurs for up to 20 s), it is likely that fragmentation is occurring prior to injection into the FT-ICR cell via various ion molecule reactions which may be occurring. Furthermore, the ^1H NMR spectrum of **G3′-Ru$_{72}$** is inconsistent with the structure shown below.



A

The difficulties in obtaining definitive mass spectral data for **G3′-Ru$_{72}$** led us to examine this material by ESI time-of-flight (ESI-TOF) mass spectrometry. The ESI-TOF spectra, after maximum entropy transformation, revealed a multitude of peaks in the range of 29600−43000 Da corresponding to singly charged species, some of which appeared to contain coordinated solvent. We attribute these peaks to the expected product, along with lower molecular weight dendrimers (e.g., the benzyl-terminated dendrimers derived from incomplete hydrosilation of **G2′-Vi$_{36}$**). Since we expect that the steric congestion at the periphery of **G3′-Ru$_{72}$** is significant, we cannot rule out the possibility that some of the peaks in the ESI-TOF spectrum also correspond to incomplete Cp^*Ru^+ functionalization (e.g., **G3′-Ru$_{71}$**). Thus, we believe that the combination of the ^1H NMR spectra and the low-resolution ESI and ESI-TOF data provide strong experimental support for the isolation of **G3-Ru$_{72}$**, with a nominal charge of 72+.

Conclusions

Four new neutral carbosilane dendrimers have been synthesized as precursors to highly charged organometallic dendrimers. The corresponding charged dendrimers, capped by Cp^*Ru^+, bear charges of 12+, 24+, 36+, and 72+. The dendrimer **G1-Ru$_{12}$**, characterized by single-crystal X-ray diffraction, has a diameter of approximately 23−28 Å. Electrospray ionization Fourier transform mass spectrometry allowed us to provide unequivocal evidence for the nuclearities of **G1-Ru$_{12}$**, **G2-Ru$_{24}$**, and **G2-Ru$_{36}$** by complete resolution of the individual isotopic distributions of the observed charge states. Although the ESI FT-ICR data for **G3-Ru$_{72}$** did not provide clear-cut evidence for its expected nuclearity, the corresponding ^1H NMR, low-resolution ESI, and ESI-TOF data suggest that the desired product has indeed been synthesized. To our knowledge, the charged dendrimers reported in this paper are the largest transition metal

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(19) Fragmentation in charged dendrimer species has been observed previously: Hong, B.; Thoms, T. P. S.; Murfee, H. J.; Lebrun, M. J. *Inorg. Chem.* **1997**, *36*, 6146.

complexes thus far characterized by ESI mass spectrometry. We are presently attempting to combine the organometallic polycations reported herein with various polyanions, in the synthesis of new superlattice materials. The results of these studies will be reported in a subsequent publication.

Experimental Section

General. All reactions were performed under an inert dinitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from purple sodium−benzophenone ketyl, CH_2Cl_2 and $ClCH_2CH_2Cl$ were distilled from CaH_2, and CH_3NO_2 was distilled from $CaCl_2$. Chloroplatinic acid was purchased from Strem Chemical Co. and used as a 0.1 M solution in dry 2-propanol. Karstedt's catalyst was purchased from United Chemical Co. as a 5% solution in xylenes and stored under nitrogen. Trichlorosilane and chlorodimethylsilane were obtained from Aldrich and distilled under nitrogen before use. The compounds $[Cp^*Ru(NCMe)_3]^+OTf^-$,[12] tetraallylsilane (**G0-Al$_4$**),[11a] and dodecaallylsilane (**G1-Al$_{12}$**)[11a] were prepared according to literature procedures. Vinylmagnesium bromide was prepared according to a literature procedure.[20] NMR spectra were recorded on a Bruker AMX (300 MHz) or a Bruker DRX (500 MHz) spectrometer.

MALDI-TOF Mass Spectrometry. The MALDI-TOF mass spectra were acquired using a Micromass TofSpec (Micromass Inc., Beverly, MA) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The instrument was operated in the linear mode at an accelerating voltage of 23 000 V. External calibration was performed using gramicidin S and insulin, with α-cyano-4-hydroxycinnamic acid serving as the matrix. Detection was by means of a microchannel plate detector and a digitizing oscilloscope operating at 250 MHz. Sample solutions with an approximate concentration of 1 mM in methylene chloride were prepared. The matrix was *trans*-3-indoleacrylic acid[21] in THF (0.2 M). One microliter of a solution prepared by combining 20 μL of matrix solution and 5 μL of sample solution was placed on the stainless steel MALDI target and analyzed following evaporation of the solvents. For dendrimers **G1-Bz$_{12}$** and **G2′-Vi$_{36}$**, silver trifluoroacetate was added to the matrix in an effort to enhance the signal intensity.[21] Thus, the corresponding molecular ions appear as $(M + Ag)^+$, not as the usual $(M + Na)^+$.

Low-Resolution ESI Mass Spectrometry. The low-resolution ESI mass spectra were acquired on a VG Quattro II (Micromass Inc., Beverly, MA) triple quadrupole instrument. The samples were delivered by a syringe pump (Harvard Apparatus, South Natick, MA) at a flow rate of 4 μL/min. Typical ionization parameters were capillary 3.8 kV, counter electrode 0.8 kV, cone 45 V, rf lens 1.7 V, skimmer 0.2 V and skimmer lens offset 5 V. The source temperature was set to 70 °C, and a resolution of 15/15 was used during all experiments. All samples were dissolved in a methanol/chloroform mixture (1:1, v/v) at a concentration of 500 mM. Solvents (HPLC grade) were obtained from Fisher Scientific (Pittsburgh, PA).

High-Resolution ESI FT-ICR Mass Spectrometry. The high-resolution ESI FT-ICR mass spectra were acquired with the National High Magnetic Field Laboratory's (Tallahassee, FL) home-built 9.4 T instrument configured for external accumulation.[22,23] Samples were infused from a tapered 50 μm i.d. fused silica microelectrospray ionization[24] needle at 500 nL min^{-1} at a concentration of 10 mM. Typical ESI conditions were 3.0 kV needle voltage and 3.5 A heated capillary current. Ions were accumulated in a linear octapole ion trap (1.0 MHz) for 20 s and then transmitted to a three-section open cylindrical 4 in. diameter Penning trap (trapping voltage, 2 V) through a second octapole ion guide. The ions were subjected to frequency sweep excitation (41−96 kHz at 300 Hz/μs) and direct-mode broadband detection (512 Kword data points and 96 kHz Nyquist bandwidth). Typical chamber base pressure was $(1-5) \times 10^{-9}$ Torr. All experiments were controlled by an Odyssey data station (Finnigan Corp., Madison, WI). All experimental time-domain transients were subjected to baseline correction, Hanning apodization, and one zero fill prior to FFT and magnitude computation.

Table 1. Crystallographic Data for G1-Ru$_{12}$

empirical formula	$C_{228}H_{288}F_{36}O_{36}Ru_{12}S_{12}Si_5$
formula wt	6028.81
crystal color, habit	brown, block
crystal dimensns	0.20 × 0.10 × 0.05 mm
crystal system	orthorhombic
a	53.8055(10) Å
b	40.8133(11) Å
c	48.1613(12) Å
V	105761(4) Å^3
Z	16
D_{calc}	1.515 g/cm^3
F_{000}	48 945
m(Mo Kα)	0.71 mm^{-1}
no. of reflctns measd	total: 109 348
unique reflctns	32 313
no. observns	32 306
no. variables	2957
R indices ($I > 2.00\sigma(I)$)[a]	R1 = 0.0789, wR2 = 0.1774
R indices (all data)[a]	R1 = 0.1316, wR2 = 0.2133
goodness-of-fit indicator, on F^2	1.193

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$. $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/\{\sigma^2(F_o^2) + [0.1((F_o^2 + 2F_c^2)/3)]^2\}$.

Crystal Structure Determination. X-ray quality crystals of **G1-Ru$_{12}$** were grown by slow vapor diffusion of Et_2O into a CH_2Cl_2 solution of the dendrimer.

Cell constants were obtained from a least-squares refinement using the measured positions of 8192 reflections in the range $2.00 < 2\theta < 46.5°$. During data collection, the temperature was −155 ± 28 °C. Area detector frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.38 and a total measuring time of 30 s each. The data were corrected for Lorentz and polarization effects. No decay correction was necessary. An empirical absorption correction based on the measurement of redundant and equivalent reflections and an ellipsoidal model for the absorption surface was applied using XPREP ($T_{max} = 0.942$, $T_{min} = 0.539$). Of the 109 348 reflections which were collected, 32 313 were unique ($R_{int} = 0.0907$); equivalent reflections were merged.

The structure was initially solved by direct methods using the teXsan software package (Table 1). The remaining structure solution and refinement were performed using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, except for the disordered solvent. Hydrogen atoms were included but not refined. The final cycle of full-matrix-block least-squares refinement was based on all 32 306 unique reflections and 2957 variable parameters and converged (largest parameter shift was 0.243 times its esd) with conventional unweighted and weighted agreement factors of R1 = 0.0789 and wR2 = 0.1774 for $I > 2\sigma(I)$. Each block included all 12 ruthenium atoms. Blocks 1−4 also contained the central silicon, and additionally, each contained the carbon and silicon atoms for one arm of the dendrimer. The final block contained the triflate molecules and the atoms corresponding to the disordered solvent. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.949 and −0.645 e$^-$/Å^3, respectively.

All Cp* and phenyl ligands were modeled as rigid groups and constrained to be flat. Further, the distance between each Ru and its ligated phenyl ring was constrained to be equal within a standard deviation of 0.03. The distance between each Ru and its Cp* ligand was constrained to be equal within a standard deviation of 0.03. The bond lengths in all 12 triflates were restrained to appropriate fixed values. The carbon thermal parameters for the Cp* and phenyl groups were subject to a restraint based on the components of the displacement parameters in the direction of the bonds. Three triflates were modeled as disordered. The disordered atoms Ru(3), Ru(4), and Ru(11) were

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(21) Leon, J. W.; Fréchet, J. M. *Polym. Bull.* **1995**, *35*, 449.

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(24) Emmett, M. R.; Caprioli, R. M. *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 605.

each modeled over two sites. The final occupation of these atoms was Ru(3)/Ru(14) 9/1, Ru(4)/Ru(15) 9/1, and Ru(11)/Ru(13) 9/1. Each asymmetric unit contained some residual electron density which was modeled as disordered solvent.

G1-Bz$_{12}$. To a thick-walled vessel with a Teflon stopcock was added 0.94 g (4.9 mmol) of tetraallylsilane (**G0-Al$_4$**) under an N_2 counterflow. The vessel was then degassed and back-filled with N_2 three times. THF (ca. 10 mL) was then added to the flask, followed by 3.00 mL (29.3 mmol) of $HSiCl_3$. To this solution was added 15 μL of a 0.1 M solution of CPA, and the vessel was then immediately sealed. The solution initially became cloudy, but after several minutes it had clarified. As soon as the catalyst was added, the reaction vessel was submersed in an oil bath at 40 °C. It was removed periodically to mix the reactants by shaking. After 15 min the reaction solution was stirred at room temperature for ca. 0.5 h and then heated again at 40 °C for 3.5 h before being allowed to cool to room temperature. An aliquot was removed for ^{1}H NMR analysis, which revealed that the starting material had been completely converted to product. The reaction solvent was removed under vacuum (over ca. 8 h). Fresh THF (ca. 110 mL) was then added to the reaction flask, and this mixture was added over 1.25 h to 74 mL of a 1.0 M benzyl Grignard solution in diethyl ether (74.0 mmol). The resulting reaction mixture was refluxed for 24 h and was then quenched with 300 mL of saturated aqueous NH_4Cl. The aqueous solution was extracted with Et_2O (2 × 100 mL), and the combined organic material was washed with H_2O and saturated aqueous NaCl (200 mL each) and then dried over $MgSO_4$. The extraction solvent was removed on a rotary evaporator to leave a yellow oil (crude yield = ca. 100%). The crude oil was purified by flash chromatography using a 20:1 hexanes/EtOAc mobile phase. The product was further purified by dissolving it in Et_2O (ca. 10 mL), adding hexanes (40 mL), and then allowing the mixture to sit at -10 °C for 8 h. The dendrimer oil separated from the organic solvents and was dried in vacuo over 3 h to leave 4.96 g (3.5 mmol, 71%) of a colorless oil. ^{1}H NMR (benzene-d_6): δ 0.43 (t, 2 H), 0.66 (t, 2 H), 1.20 (m, 2 H), 2.12 (s, 6 H), 6.92, 6.95, 6.96, 6.98, 7.10, 7.12 (Ar, 15 H). ^{13}C NMR (benzene-d_6): δ 17.37, 18.10, 18.62, 22.39, 124.79, 128.73, 128.83, 139.65. MALDI-TOF MS: *m*/*z* calcd for $Si_5C_{96}H_{108}$ 1426.4 (M + Na), found 1426.0 (M + Na).

G1-Ru$_{12}$. The dendrimer **G1-Bz$_{12}$** (0.155 g, 0.109 mmol) in CH_2Cl_2 (ca. 50 mL) was transferred to a reaction vessel containing 0.667 g (12.1 equiv, 1.32 mmol) of [Cp*Ru(NCMe)$_3$]OTf and equipped with a Teflon stopcock. The reaction mixture was heated for 2 h at 50 °C and then filtered. The filtrate was concentrated to about 1/6 of its original volume, and then Et_2O was added (ca. 25 mL). The resulting tan precipitate was isolated by filtration and then washed with two 10 mL portions of Et_2O to yield 0.555 g (85% yield) of the title compound. ^{1}H NMR ($CDCl_3$): δ -0.61 (br, 2 H), 0.15 (br, 2 H), 0.87 (br, 2 H), 1.96 (s, 45 H), 2.17 (s, 6 H), 5.78 (m, 15 H). ^{13}C NMR ($CDCl_3$): δ 10.18, 17.20, 17.35, 17.84, 19.10, 86.15, 86.81, 96.01, 104.56, 122.52 (quartet corresponding to O_3SCF_3). ESI-MS (*m*/*z*): 1357 [M $-$ 4OTf]$^{4+}$, 1860 [M $-$ 3 OTf$^-$]$^{3+}$. ESI FT-ICR (*m*/*z*): 1357.8 [M $-$ 4OTf$^-$]$^{4+}$, 1860.4 [M $-$ 3OTf]$^{3+}$.

G2-Bz$_{36}$. The synthetic procedure was similar to that used for **G1-Bz$_{12}$**, with 1.00 g (1.25 mmol) of dodecaallylsilane (**G1-Al$_{12}$**), 2.00 mL (20.0 mmol) of $HSiCl_3$ and 45 μL of CPA for the hydrosilation, and 55 mL of benzyl Grignard (1.0 M solution in diethyl ether; 55.0 mmol). The crude yellow oil (crude yield = 100%) was purified by flash chromatography using a 50:50 hexanes/CH_2Cl_2 mobile phase. The product was further purified by dissolving it in Et_2O (ca. 10 mL), adding pentane (40 mL), and then allowing this mixture to sit at 25 °C for 1 h. The dendrimer oil separated from the organic solvents and was dried in vacuo over 3 h to leave 3.60 g (65%) of a colorless oil. ^{1}H NMR (benzene-d_6): δ 0.52 (t, 6 H), 0.67 (t, 6 H), 0.74 (t, 2 H), 1.16 (t, 2 H), 1.24 (m, 6 H), 1.70 (m, 2 H), 2.14 (s, 18 H), 6.95, 6.97, 7.03, 7.04, 7.06, 7.17, 7.18 (Ar, 45 H). ^{13}C NMR (benzene-d_6): δ 16.99, 17.44, 17.92, 18.09, 18.37, 18.65, 21.87, 124.28, 128.29, 128.38, 139.23. MALDI-TOF MS: *m*/*z* calcd for $Si_{17}C_{300}H_{348}$ 4453.5 (M + Na), found 4452.3 (M + Na).

G2-Ru$_{36}$. The dendrimer **G2-Bz$_{36}$** (0.30 g, 0.068 mmol) in CH_2Cl_2 (ca. 30 mL) was transferred to a reaction vessel containing 1.27 g (37.0 equiv, 2.51 mmol) of [Cp*Ru(NCMe)$_3$]OTf and equipped with a Teflon stopcock. The reaction mixture was heated for 3 d at 65 °C; the solvent was removed in vacuo, fresh CH_2Cl_2 was added, and heating was then commenced at least 15 times during this time. The reaction mixture was filtered, the filtrate was concentrated to about 1/4 of its original volume, and then Et_2O was added (ca. 25 mL). The resulting tan precipitate was isolated by filtration and washed with two 30 mL portions of Et_2O to yield 1.20 g (81%) of the title compound. ^{1}H NMR (CD_3NO_2): δ 1.00 (br), 2.05 (br), 2.15 (br), 5.78 (br). ^{13}C NMR (CD_3NO_2): δ 11.18, 20.0 (br), 88.14 (br), 97.86 (br), 121.35 (quartet corresponding to O_3SCF_3). ESI-MS (*m*/*z*): (**G2-Ru$_{36}$**) 2468 [M $-$ 7OTf]$^{7+}$, 2901 [M $-$ 6OTf]$^{6+}$, 3513 [M $-$ 5OTf]$^{5+}$; (**G2-Ru$_{35}$**) 2412 [M $-$ 7OTf]$^{7+}$, 2838 [M $-$ 6OTf]$^{6+}$, 3436 [M $-$ 5OTf]$^{5+}$. ESI FT-ICR (*m*/*z*): (**G2-Ru$_{36}$**) 2139.0 [M $-$ 8OTf]$^{8+}$, 2465.8 [M $-$ 7OTf]$^{7+}$, 2902.0 [M $-$ 6OTf]$^{6+}$, 3512.4 [M $-$ 5OTf]$^{5+}$; (**G2-Ru$_{35}$**) 2090.9 [M $-$ 8OTf]$^{8+}$, 2410.7 [M $-$ 7OTf]$^{7+}$, 2837.6 [M $-$ 6OTf]$^{6+}$, 3434.5 [M $-$ 5OTf]$^{5+}$.

G2-Bz$_{24}$. The synthetic procedure was similar to that used for **G1-Bz$_{12}$**, with 1.06 g (1.32 mmol) of dodecaallylsilane (**G1-Al$_{12}$**), 2.20 mL (21.2 mmol) of $HSiMeCl_2$ and 45 μL CPA for the hydrosilation, and 40 mL of benzyl Grignard (1.0 M solution in diethyl ether; 40.0 mmol). The crude oil was purified by flash chromatography using a 50:50 hexanes/CH_2Cl_2 mobile phase. The product was further purified by dissolving it in Et_2O (ca. 10 mL), then adding pentane (40 mL), and letting this mixture sit at 25 °C for 1 h. The dendrimer oil separated from the organic solvents and was dried in vacuo over 3 h to leave 3.07 g (66%) of a colorless oil. ^{1}H NMR (benzene-d_6): δ -0.10 (s, 9 H), 0.42 (t, 6 H), 0.48 (overlapping, 2 H), 0.53 (t, 6 H), 0.63 (br, 2 H), 1.18 (m, 6 H), 1.28 (br, 2 H), 2.05 (s, 12 H), 6.93 (d, 12 H), 7.03 (t, 6 H), 7.16 (t, 12 H). ^{13}C NMR ($CDCl_3$): δ -5.28, 17.47, 18.01, 18.11, 18.15, 18.37, 18.57, 23.85, 124.10, 128.18, 128.23, 139.74; MALDI-TOF MS: *m*/*z* calcd for $Si_{17}C_{228}H_{300}$ 3541.3 (M + Na), found 3542.2 (M + Na).

G2-Ru$_{24}$. The dendrimer **G2-Bz$_{24}$** (0.399 g, 0.113 mmol) in CH_2Cl_2 (ca. 30 mL) was transferred to a reaction vessel containing 1.38 g (24.0 equiv, 2.72 mmol) of [Cp*Ru(NCMe)$_3$]OTf and equipped with a Teflon stopcock. The reaction mixture was heated for 1.5 h at 50 °C, the solvent was removed in vacuo, fresh CH_2Cl_2 was added, and heating was then continued for another hour. The reaction mixture was filtered, the filtrate was concentrated to about 1/4 of its original volume, and then Et_2O was added (ca. 25 mL). The resulting tan precipitate was isolated by filtration and washed with two 30 mL portions of Et_2O to yield 1.20 g (83% yield) of the title compound. ^{1}H NMR (CD_3NO_2): δ 0.10 (s, 9 H), 0.51 (br, 10 H), 0.81 (br, 6 H), 1.23 (br, 8 H), 1.97 (s, 90 H), 2.05 (s, 6 H), 5.73 (m, 30 H). ^{13}C NMR (CD_3NO_2): δ -5.25, 10.83, 18.38, 18.41, 18.93, 18.95, 19.57, 21.48, 87.42, 87.94, 88.02, 88.15, 97.44, 122.53 (quartet corresponding to O_3SCF_3) ESI-MS (*m*/*z*): 1675 [M $-$ 7OTf$^-$]$^{7+}$, 1979 [M $-$ 6OTf]$^{6+}$, 2406 [M $-$ 5OTf$^-$]$^{5+}$, 3044 [M $-$ 4OTf]$^{4+}$. ESI FT-ICR (*m*/*z*): 1675.1 [M $-$ 7OTf$^-$]$^{7+}$, 1979.4 [M $-$ 6OTf]$^{6+}$, 2404.7 [M $-$ 5OTf$^-$]$^{5+}$, 3043.2 [M $-$ 4OTf]$^{4+}$.

G2-Vi$_{36}$. The synthetic procedure was similar to that used for **G1-Bz$_{12}$**, with 1.00 g (1.25 mmol) of dodecaallylsilane (**G1-Al$_{12}$**) and 8.40 mL (83.3 mmol) of $HSiCl_3$ and 180 μL of CPA for the hydrosilation. During this time, to 5.35 g (220 mmol) of activated Mg powder was added 14.7 mL (208 mmol) of freshly condensed vinyl bromide in THF (150 mL) according to literature procedures.[18] Freshly generated vinylmagnesium bromide (excess, in tetrahydrofuran) was added as soon as the hydrosilation was determined to be complete (by ^{1}H NMR spectroscopy of an aliquot). The crude oil was purified by flash chromatography using a 3:1 hexanes/CH_2Cl_2 mobile phase. The product was further purified by dissolving it in Et_2O (ca. 10 mL), then adding pentane (40 mL), and letting this mixture sit at 25 °C for 1 h. The dendrimer oil separated from the organic solvents and was dried over 3 h in vacuo to leave 4.74 g (48%) of a slightly yellow oil. ^{1}H NMR ($CDCl_3$): δ 0.53 (t, 2H), 0.58 (t, 6 H), 0.81 (t, 6 H), 1.26 (m, 2 H), 1.24 (m, 6 H), 1.40 (m, 2 H, overlapping methylenes), 5.74$-$5.79 (m, 9 H), 6.06$-$6.18 (m, 18 H); ^{13}C NMR ($CDCl_3$): δ 17.45, 17.57, 17.73, 18.02, 18.38, 18.57, 134.20, 134.88. MALDI-TOF MS: *m*/*z* calcd for $Si_{17}C_{120}H_{204}$ 2232 (M + Ag), found 2231 (M + Ag).

G3-Bz$_{72}$. The synthetic procedure was similar to that used for **G1-Bz$_{12}$**, with 0.74 g (0.35 mmol) of **G2-Vi$_{36}$**, 1.60 mL (15.3 mmol) of

$HSiMeCl_2$ and 40 μL CPA for the hydrosilation, and 40 mL of benzyl Grignard (1.0 M solution in diethyl ether; 55.0 mmol). The crude oil was purified by flash chromatography using a 50:50 hexanes/CH_2Cl_2 mobile phase. The product was further purified by dissolving it in Et_2O (ca. 10 mL), then adding pentane (40 mL), and letting this mixture sit at 25 °C for 1 h. The dendrimer oil separated from the organic solvents and was dried over 2 h in vacuo to leave 2.00 g (56%) of a colorless foamy glass. ^{1}H NMR (benzene-d_6): δ 0.06 (s, 27 H), 0.53 (br overlapping, 36 H), 0.83 (br, 6 H), 0.99 (br, 8 H), 1.19 (br, 2 H), 1.62 (br, 6 H), 1.83 (br, 2 H), 2.17 (s, 36 H), 7.02−7.25 (Ar, 45 H). ^{13}C NMR (benzene-d_6): δ -4.87, 4.06, 6.16, 18.42, 18.98, 19.83 (the three innermost carbons were not resolved), 24.06, 125.11, 129.05, 129.18, 140.43. MALDI-TOF MS: *m/z* calcd for $Si_{17}C_{228}H_{300}$ 10297.5 (M + Na), found 10296.4 (M + Na) and peaks corresponding to one and two incomplete hydrosilations, respectively, at 10072.9 (M + Na) and 9847.9 (M + Na).

G3-Ru$_{72}$. The dendrimer **G3-Bz$_{72}$** (0.109 g, 0.0106 mmol) in $ClCH_2CH_2Cl$ (ca. 20 mL) was transferred to a reaction vessel containing 0.485 g (90.0 equiv, 0.995 mmol) of [Cp*Ru(NCMe)$_3$]OTf and equipped with a Teflon stopcock. The reaction mixture was heated for 3 d at 95 °C. During this time, the solvent was periodically removed under vacuum, and fresh $ClCH_2CH_2Cl$ solvent was added (20 times in total), to remove acetonitrile from the reaction solution. The reaction mixture was filtered, the filtrate was concentrated to about 1/4 of its original volume, and then Et_2O was added (ca. 25 mL). The resulting tan precipitate was isolated by filtration and washed with three 30 mL portions of Et_2O and two 20 mL portions of pentane to yield 0.361 g (89% yield) of the title compound. ^{1}H NMR (CD_3NO_2): δ 0.52 (br), 1.98 (br), 2.02 (br), 5.77 (br). ESI-MS (*m/z*): 1208 $[M - 28OTf^-]^{28+}$, 1434 $[M - 24OTf]^{24+}$, 1751 $[M - 20OTf]^{20+}$, 2225 $[M - 16OTf]^{16+}$. ESI FT-ICR (*m/z*): 1752.0 $[M - 5OTf]^{5+}$, 2225.4 $[M - 4OTf]^{4+}$, 3017.6 $[M - 3OTf]^{3+}$. ESI-TOF: singly charged ions at 42986, 40028, 39198, 38469, 38072, 37521, 36769, 35659, 34972, 33574, 33205, 31673, 29603.

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Supporting Information Available: Low-resolution ESI spectra for **G2-Ru$_{36}$**, FT-ESI spectra showing all the observed isotopic distributions for **G1-Ru$_{12}$**, **G2-Ru$_{36}$**, **G2-Ru$_{24}$**, and **G3′-Ru$_{72}$**, ESI-TOF spectra for **G3′-Ru$_{72}$**, tables of positional and thermal parameters, bond lengths and angles, and torsion angles, and an ORTEP drawing of **G1-Ru$_{12}$** (45 pages, print/PDF). See any current masthead page for ordering and Internet instructions.

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