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Organoruthenium Dendrimers

Yi-Hsien Liao and John R. Moss*

Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa

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We describe the synthesis of a series of very large organometallic dendrimers. These dendrimers have been prepared by the convergent approach and contain organometallic functional groups, namely $Cp(CO)_2RuCH_2CH_2CH_2O-$ ($Cp = \eta^5\text{-}C_5H_5$), which lie exclusively at the periphery of the dendritic structure. The construction of these dendrimers starts by the reaction of the (bromopropyl)ruthenium complex $[CpRu(CO)_2\{(CH_2)_3Br\}]$ with the building block 3,5-dihydroxybenzyl alcohol. This reaction gives the first generation dendritic wedge with a benzyl alcohol functional group at the focal point. The benzyl alcohol functional group can then be activated by the reaction with a PPh_3/CBr_4 mixture to give the dendritic wedge with a benzyl bromide functional group. This first generation dendritic wedge reacts with 3,5-dihydroxybenzyl alcohol to give a dendritic wedge of the second generation; it will also react with the trifunctional core molecule 1,1,1-tris(4′-hydroxyphenyl)ethane to give the first generation dendrimer. Through consecutive reaction cycles, we have prepared dendritic wedges up to the fourth generation. This fourth generation dendritic wedge reacts with 1,1,1-tris(4′-hydroxyphenyl)ethane to give a fourth generation dendrimer, which contains 48 ruthenium metal atoms and has a nominal molecular weight of 18 438 amu. The characterization data and thermal properties of the dendrimers and the dendritic wedges are reported and discussed.

Introduction

"Modern chemistry, like modern architecture, deals with structures whose design is constrained by natural forces, as well as depending on their eventual use."[1] Particularly in the history of polymer science, the development of controlled polymerization methodology has enabled polymers to be synthesized so as to exhibit specific properties such as defined molecular weight, narrow molecular weight distribution, pendant and end functional group, and main chain stereoregularity.[2] However, in terms of molecular topology, the traditional polymers are linear in shape and exist as random coils in solution.

Recently, there has been a growing interest in synthesizing highly branched polymers with well-defined three-dimensional structures. The shapes of molecules, which are carefully controlled by a series of elaborate synthetic strategies, can be either comblike, starlike, or even treelike. The treelike polymers are also known by various names, such as dendrimer (*dendron*: Greek, tree), arborol (*arbor*: Latin, tree), cascade molecules, or starburst polymers, and it is this type of polymer that has attracted particular attention in recent years.[3] Several review articles on dendrimers have been published recently.[2,4] The reason for interest in dendrimers is that their molecular architecture is so different from the traditional linear polymers. Perhaps the most distinctive feature of dendrimers is their rigid highly branched structure and the huge numbers of chain ends (normally hundreds) that lie exclusively on the surface of the molecules. Therefore, one can expect that the functional groups on the chain ends would play an important role in the physical properties of these polymers, such as solubility in organic solvents or the glass transition temperature. Generally speaking the dendrimers are prepared by controlled stepwise methods. This requires a very carefully designed synthetic strategy, and chain propagation occurs by repeated coupling and activation reactions. Thus, an ideally branched dendrimer would have a specific molecular weight and would be monodispersed. The direction of chain propagation in dendrimers can be either outward (the divergent approach)[5] or inward (the convergent approach).[6] A comparison of the divergent approach and the convergent approach is briefly summarized in Table 1.

Many dendritic polymers have been reported in recent years. However, the majority are organic in nature.

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* To whom correspondence should be addressed.

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(1) Hoffmann, R. *New Scientist* **1990**, *128*, 44.

(2) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.

(3) Kim, Y. H. *Adv. Mater.* **1992**, *4*, 764; *Chem. Brit.* **1993**, *29*, 460. Hodge, P. *Nature* **1993**, *362*, 18. O'Sullivan, D. A. *Chem. Eng. News* **1993**, Aug 16, 20. Tomalia, D. A.; Dvornic, P. R. *Nature* **1994**, *372*, 617. Tomalia, D. A. *Sci. Am.* **1995**, May, 62. DeSimone, J. M. *Science* **1995**, *269*, 1060. Newkome, G. R., Ed. *Advances in Dendritic Macromolecules*; JAI Press: Greenwich, CT, 1994−1996.

(4) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem.. Int. Ed. Engl.* **1990**, *29*, 138. Mulzer, J., *et al.*, Eds. *Organic Synthesis Highlights*; VCH: Weinheim, Germany, 1991; pp 378−383. Tomalia, D. A.; Durst, H. D. In Topics in Current Chemistry, Vol. 165. *Supramolecular Chemistry I: Directed Synthesis and Molecular Recognition*; Weber, E., Ed.; Springer: Berlin, 1993; pp 193−313. Mekelburger, H.-B.; Jaworek, W.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1571. Newkome, G. R.; Moorefield, C. N.; Baker, G. R. *Aldrichim. Acta* **1992**, 25, 31. Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *Chem. Austral.* **1992**, Dec, 620. Tomalia, D. A. *Aldrichim. Acta* **1993**, *26*, 91. Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Coord. Chem. Rev.* **1994**, *132*, 1. Turro, N. J.; Barton, J. K.; Tomalia, D. A. *Acc. Chem. Res.* **1991**, *24*, 332. Voit, B. I. *Acta Polym.* **1995**, *46*, 87. Escamilla, G. H.; Newkome, G. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1937. Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413.

(5) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117. Newkome, G. R.; Yao, Z.-Q.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003.

(6) Hawker, C. J.; Fréchet, J. M. J.; Wooley, K. L. *Pure Appl. Chem.* **1994**, *A31*, 1627. Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010. Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

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Table 1. Comparison of the Divergent and the Convergent Approaches for the Synthesis of Dendrimers

advantages	disadvantages
divergent approach	
1. suitable for high MW dendrimers (>100 000)	1. large excess of reactant required
2. less reacn sequences involved	2. less control on the molecular architecture
3. large quantity production is accessible	
convergent approach	
1. block copolymers are accessible	1. MW of dendrimer is limited (<100 000)
2. reacn stoichiometry is under control	2. more elaborate reacn sequences involved

Dendritic polymers which include transition metals or main-group elements have been far less studied.[7] Here, we report the synthesis and characterization of a series of new organoruthenium dendrimers. The properties of these new materials are also described. Some of these results have been reported in preliminary communications.[8] It is hoped that these novel materials will have useful applications including use as catalysts or as precursors to metallic films.

Results and Discussion

Synthesis. The dendrimers prepared in this study are based on 3,5-dihydroxybenzyl alcohol as the monomer unit, and the organometallic functional groups, viz. $Cp(CO)_2RuCH_2CH_2CH_2O-$, are attached exclusively at the periphery of the dendrimers. The synthetic strategy adopted here is the convergent approach, as developed by Hawker and Fréchet.[6] The preparation of these new organoruthenium dendrimers starts from the (bromopropyl)ruthenium complex $[CpRu(CO)_2\{(CH_2)_3Br\}]$[9] (**1**), which will eventually become the chain-end functional group. We have previously found that the reactions of haloalkyl transition metal complexes can be directed to the halo functional groups, while the metal and its associated ligands remain intact.[10]

Thus 2 molar equiv of **1** was reacted with 1 molar equiv of 3,5-dihydroxybenzyl alcohol in the presence of potassium carbonate and 18-crown-6 in refluxing acetone for 2 days. The reaction was monitored by thin-layer chromatography (TLC), eluting with a 70% CH_2Cl_2/hexane solution. The resulting complex **2**, as shown in Scheme 1, was purified by column chromatography and recrystallization to give a reasonable yield of 70%. It has been reported that vigorous stirring throughout this type of reaction is essential in order to ensure high conversion.[6] Also, in some cases, we found that protection from light is necessary to optimize the yield of the product. Complex **2** is the first-generation benzyl alcohol complex and is a colorless crystalline solid (mp 81−84 °C).

Complex **2** was converted to the corresponding benzyl bromide complex **3** in high yield (90%) by treatment with PPh_3/CBr_4 in a minimum volume of THF (Scheme 1). This reaction is usually complete within 20 min; it was monitored by TLC, eluting with a 30% CH_2Cl_2/hexane solution. Analytically pure **3** was obtained after column chromatography and recrystallization. It was found that a large excess of PPh_3/CBr_4 is usually needed in order to achieve complete conversion in this reaction, especially in the cases of higher generation benzyl alcohol complexes. Also, in our experience, the volume of THF solvent used in the reaction has a significant effect on the yields of products, as does the quantity of PPh_3/CBr_4 required for the reaction. Complex **3** is obtained as a colorless crystalline solid (mp 107−109 °C) and is stable at room temperature.

The reaction of 2 equiv of **3** with 1 equiv of 3,5-dihydroxybenzyl alcohol gives the anticipated second-generation benzyl alcohol complex **4**, as a white glassy solid in 70% yield. Similarly, the second-generation benzyl alcohol complex **4** was converted to the analogous benzyl bromide complex **5** by reacting with PPh_3/CBr_4.

These new organoruthenium dendrimers proved difficult to purify, partly because they are highly soluble in common organic solvents, except hexane, and sparingly soluble in methanol. In the recrystallization process, these dendritic polymers usually separate out as oils rather than solids, and the resulting glassy solid can only be obtained after drying under high vacuum. We find that, in some cases, column chromatography followed by several recrystallizations may be needed in order to obtain products that are sufficiently pure for the subsequent reactions.

The third- and fourth-generation dendritic wedges *viz.* **6**−**9** (Chart 1) are prepared in a similar fashion to their earlier generation analogues. It was found that the yields of reactions decrease slightly as the size of the dendrimers grow. This may be due to the increasing steric congestion around the focal points of the dendritic wedges, which reduces the reactivity of functional groups at the focal point. In this study, we have prepared organoruthenium dendritic wedges up to the fourth generation, i.e. **8** and **9**, containing 16 ruthenium atoms, with nominal molecular weights of about 6000.

In the convergent approach, the dendritic wedges containing benzyl bromide functional groups can be reacted with a polyfunctional CORE molecule; in this paper, the chosen trifunctional CORE molecule is 1,1,1-tris(4′-hydroxyphenyl)ethane. This reaction is similar to the one used in building the benzyl alcohol dendritic wedges. Thus in a typical reaction, 3 molar equiv of the benzyl bromide dendritic wedges are reacted with 1 molar equiv of the CORE molecule in the presence

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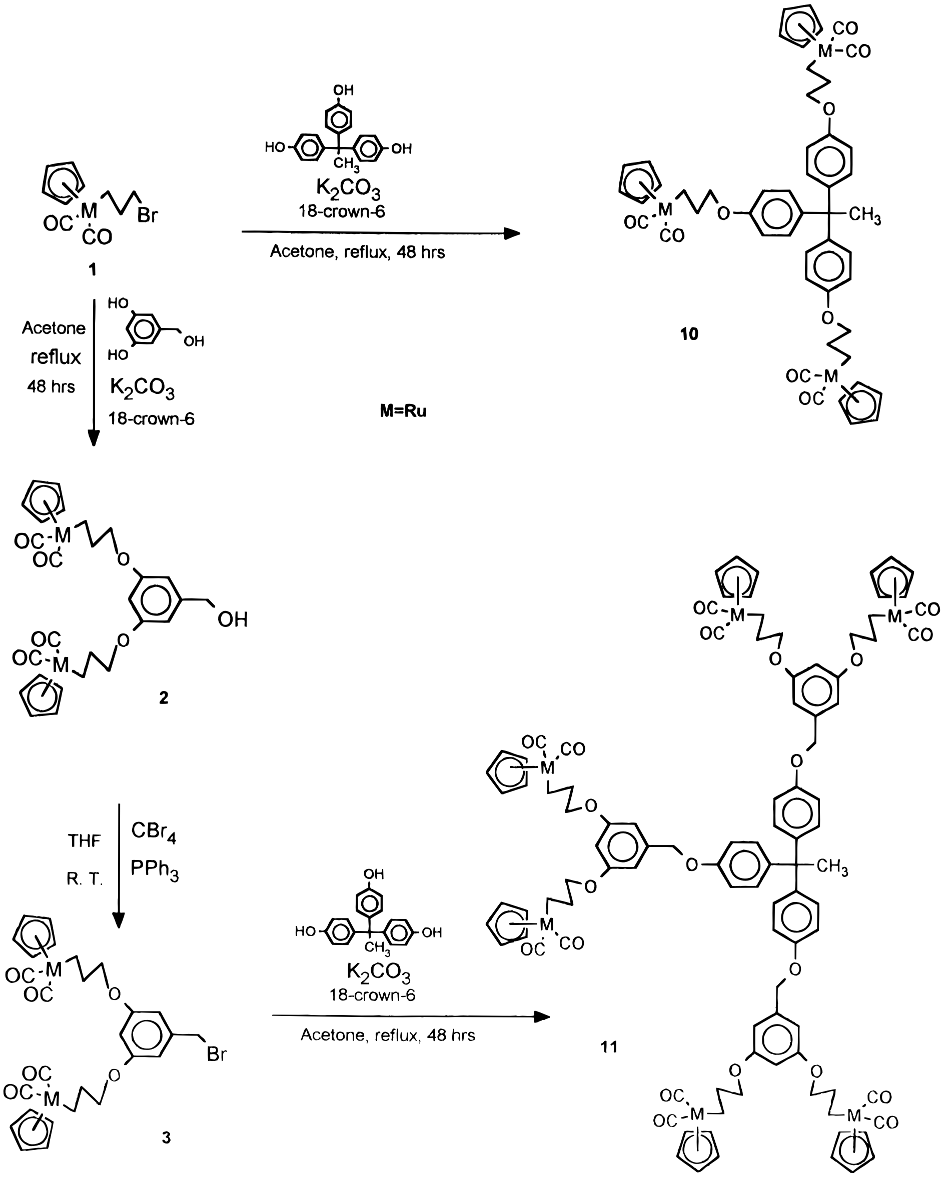
(7) See for example: Bochkarev, M. N. *Metalloorg. Khim. (USSR)* **1988**, *1*, 115. Serroni, S.; Denti, G.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1493. Newkome, G. R.; Cardullo, F.; Constable, E. C.; Moorefield, C. N.; Cargill Thompson, A. M. W. *J. Chem. Soc., Chem. Commun.* **1993**, 925. Newkome, G. R.; Moorefield, C. N.; Keith, J. M.; Baker, G. R.; Escamilla, G. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 666. Moulines, F.; Djakovitch, L.; Boese, R.; Gloaguen, B.; Thiel, W.; Fillaut, J.-L.; Delville, M.-H.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1075. van der Made, A. W.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400. Zhou, L.-L.; Roovers, J. *Macromolecules* **1993**, *26*, 963. Rengan, K.; Engel, R. *J. Chem. Soc., Perkin Trans. I*, **1991**, 987. Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J.; Wudl, F.; Srdanov, G.; Shi, S.; Li, C.; Kao, M. *J. Am. Chem. Soc.* **1993**, *115*, 9836. Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 925. Jin, R.-H.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1260. Achar, S.; Puddephatt, R. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 847. Achar, S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 43. Huck, W. T. S.; van Veggel, C. J. M.; Kropman, B. L.; Blank, D. H. A.; Keim, E. G.; Smither, M. M. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 8293.

(8) Liao, Y.-H.; Moss, J. R. *J. Chem. Soc., Chem. Commun.* **1993**, 1774. Liao, Y.-H.; Moss, J. R. *Organometallics* **1995**, *14*, 2130.

(9) Friedrich, H. B.; Finch, K. P.; Gafoor, M. A.; Moss, J. R. *Inorg. Chim. Acta* **1993**, *206*, 225.

(10) Friedrich, H. B.; Makhesha, P. A.; Moss, J. R.; Williamson, B. K. *J. Organomet. Chem.* **1990**, *384*, 325.

Scheme 1



of potassium carbonate and 18-crown-6 in refluxing acetone for 48 h. Some representative reactions are shown in Scheme 1. The resulting products, **10**−**14**, were purified by column chromatography and recrystallization.

In the case of the fourth generation, however, the resulting product **14** and the starting complex **9** could not be separated by column chromatography. To solve this problem, a slight excess of **9** was used (3.3 equiv) to react with one molar equivalent of the CORE molecule. Once the reaction was complete (after two days), a large excess of the CORE molecule (*ca.* 15 equiv) was added to react with any excess of **9**. The resulting monoalkylated CORE complex still containing two phenolic functional groups has significantly different polarity in column chromatography compared to the desired product **14**. Thus **14** can now be purified by column chromatography and was obtained in 70% yield after recrystallization. As far as we know, **14** is the largest organotransition metal complex ever reported. It contains 48 ruthenium metal atoms at the chain-ends and has a nominal molecular weight of 18 438 amu. The diameter of **14**, estimated by a computer-assisted molecular model, is about 5 nm.[11]

All the ruthenium dendrimers described here are air stable in the solid or glassy state but slowly decompose in solution within a few hours on exposure to air.

IR Spectroscopy. The IR spectra of **2**−**14** were recorded in a CH_2Cl_2 solution between 2200 and 1600 cm^{-1}. All these organoruthenium dendrimers showed two strong ν(CO) bands at 2012 and 1957 cm^{-1}, which is exactly the same position as for $[CpRu(CO)_2\{(CH_2)_3Br\}]$. It was anticipated that the densely packed chain-ends might have had an effect on the ν(CO) absorption bands; however, neither band shift nor band distortion was observed in any of these dendrimers.

Elemental Analysis. Satisfactory elemental analysis results (C, H) were obtained for all of the new dendrimers. However, the elemental analysis is not sufficiently accurate to distinguish between some of the dendrimers. For example, **4** requires C = 51.0%, H = 4.2%, while **7** requires C = 50.8%, H = 4.1%, although these two dendrimers are very different from each other in terms of functional groups at the focal point and their generation number.

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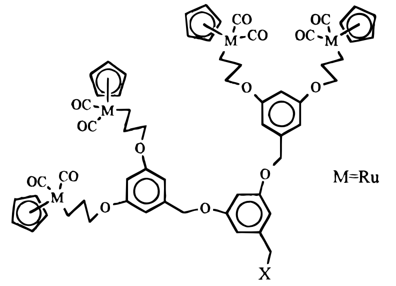
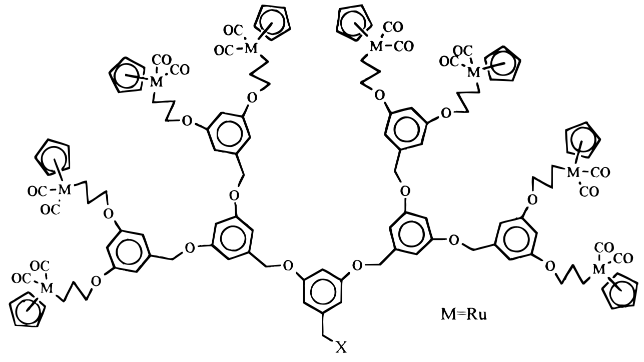
[11] The computer-assisted molecular models have been generated using BIOSYM.

Chart 1



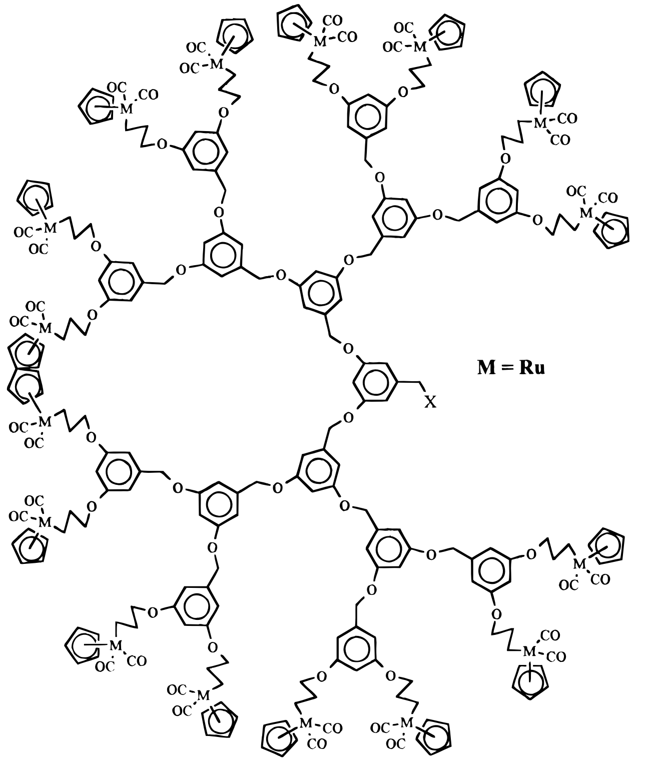
4 X=OH

5 X=Br



6 X=OH

7 X=Br



8 X=OH

9 X=Br

Mass Spectrometry. The molecular masses of the new organoruthenium dendrimers, up to about 4500 amu, were confirmed by fast atom bombardment (FAB) mass spectrometry. For the dendrimers with molecular masses below 1400, the FAB mass spectra showed molecular ion peaks at the anticipated positions. The elemental composition of molecular ion peaks was further confirmed by comparing the found and calculated isotope patterns. However, in the cases of high molecular weight dendrimers, we only observed a set of daughter peaks around the anticipated $[p - 2CO]^+$ position. The exact positions of some of these fragments in FAB mass spectra were not completely certain due to the following factors: low intensity of peaks, the complicated isotope patterns resulting from the large number of ruthenium atoms, and the possible overlapping of fragments such as $[p - 2CO - H]^+$, $[p - 2CO - 2H]^+$, *etc.* However, we believe that the mass spectra reported here are reasonable, since previous studies in this laboratory have shown that complexes of the type $[CpM(CO)_2\{(CH_2)_nX\}]$ (M = Fe, Ru; X = H, Br, I)[9,10,12] give very weak molecular ion peaks in their mass spectra. Also, the ratio of the peak intensities of $[p - 2CO]^+/[p]^+$ is found to increase as the molecular weight of the complex increases.

Several attempts have been made to observe molecular ions for the dendrimers of higher molecular mass, including the use of matrix-assisted laser desorption ionization (MALDI) mass spectrometry. However, these attempts have so far been unsuccessful.

Size-Exclusion Chromatography (SEC). Since we were only able to obtain molecular weights of the dendrimers by mass spectrometry up to about 4500 amu, we investigated the use of SEC for some of the new complexes. We found that molecular masses estimated by SEC were always lower than the nominal molecular mass. Thus, for complex **11** we obtained a molecular mass of 1299, compared to the nominal molecular mass of 2252 (supported by mass spectrometry). For complex **8**, we found a molecular mass of 2289 by SEC, compared to the nominal molecular mass of 6062. Similar results have been found by Hawker and Fréchet for dendritic benzyl ether macromolecules.[6] These results indicate that the highly branched macromolecules have a globular structure which tends to be more strongly trapped in the gel phase whereas polystyrenes used for standards should be linearly extended in solvents such as tetrahydrofuran. The polydispersity indices for **11** and **8** were found to be 1.01 and 1.04, respectively, confirming that the products are single monodisperse materials.

NMR Spectroscopy. NMR spectroscopy has proved to be invaluable in the characterization of these new dendritic compounds. All the dendrimers prepared in this study were characterized by ^1H and ^{13}C NMR spectroscopy. A 400 MHz ^1H NMR spectrum of **6** is shown in Figure 1. In all cases, the organoruthenium functional groups on the periphery of the molecules give four sets of resonances at δ 5.23 (Cp), 3.85 (CH_2O), 2.01 (CH_2), and 1.70 ($RuCH_2$) ppm. The triplet observed at δ 3.85 ppm confirms the formation of **2** from **1** at the first stage of construction of the dendrimers. The exponential growth in integration of these resonances indicates that no significant degradation of the organoruthenium functional groups occurs during the dendrimer synthesis.

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[12] Emeran, A.; Gafoor, M. A.; Goslett, J. K. I.; Liao, Y.-H.; Pimble, L.; Moss, J. R. *J. Organomet. Chem.* **1991**, *405*, 237.

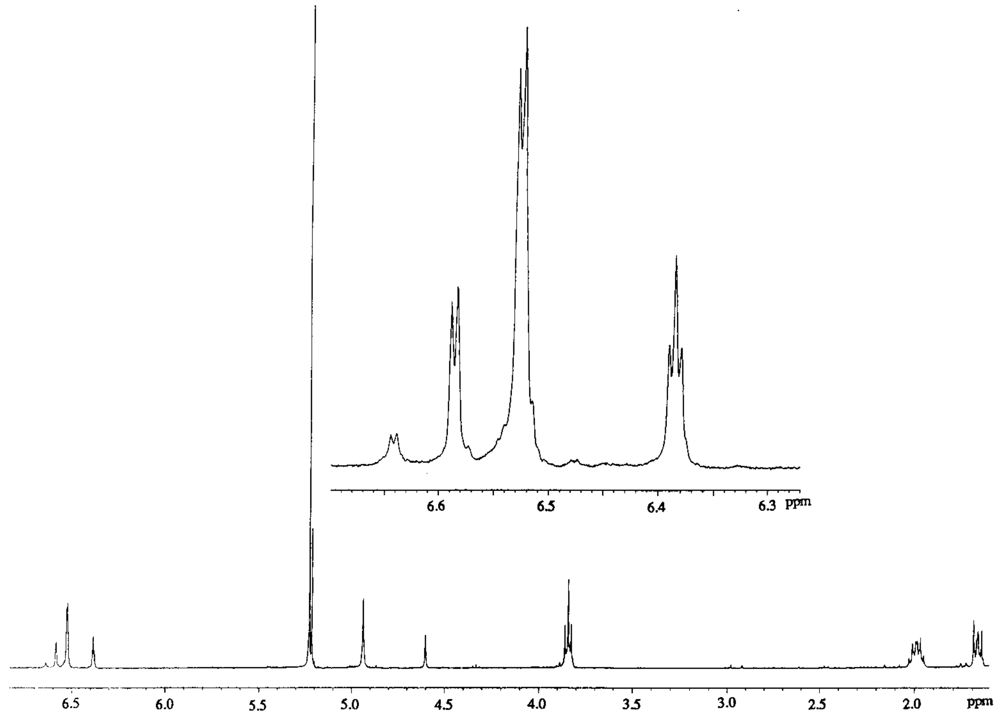

Figure 1. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **6**.

The resonances occurring in the region of δ 6.3–6.7 ppm were assigned to the aromatic protons of the dendritic building blocks. Separate resonances, corresponding to each "layer" of the dendritic wedge (with appropriate integrations) were observed. This is demonstrated in Figure 1, from which the generation number can be easily identified by the number of doublet peaks (*i.e.* three doublets were observed for the third-generation dendritic wedge **6**).

The resonances in the region of δ 4.3–5.0 ppm were assigned to the benzyl CH$_2$ protons. Again, separate resonances can be seen in the region of δ 4.9–5.0 ppm for the different "layers" of the dendritic wedges. For example, Figure 2 shows the ^{1}H NMR spectrum of the fourth-generation benzyl alcohol dendritic wedge **8** in the region of 4.5–5.1 ppm, from which the different "layers" of dendritic building blocks can clearly be seen. Perhaps the most important information one can obtain from this region of the spectrum is the resonances due to the functional groups at the focal point of dendritic wedges. The benzyl alcohol functional group gives a doublet resonance at *ca.* 4.57 ppm, whereas the benzyl bromide functional group shows a singlet resonance at *ca.* 4.40 ppm. A shift from 4.40 to 4.90 ppm of the same CH$_2$ resonance was observed when the dendritic wedges were coupled to the CORE molecule. This was accompanied by a new resonance at 2.01 ppm corresponding to methyl protons of the CORE molecule, while the aromatic protons of the CORE molecule gave two distinguishable doublets at 6.82 and 6.97 ppm. Figure 3 shows the 400 MHz ^{1}H NMR spectra of **4**, **5**, and **12** in the region of 4.4–5.0 ppm. The dramatic shifts of the focal benzyl CH$_2$ resonances in the various dendrimers can easily be seen.

In all cases, the integration of the resonances was employed to further confirm the generation number and to ascertain whether the reaction with the CORE molecule (or with 3,5-dihydroxybenzyl alcohol) had gone to completion. This is particularly important in the case of **14**, since the ^{1}H NMR spectrum showed significantly broadened signals and no mass spectrum could be obtained for this complex. Confirmation of the formation of **14** is thus made by a comparison of the integrations of the aromatic protons of the CORE unit with those of the dendritic building blocks.

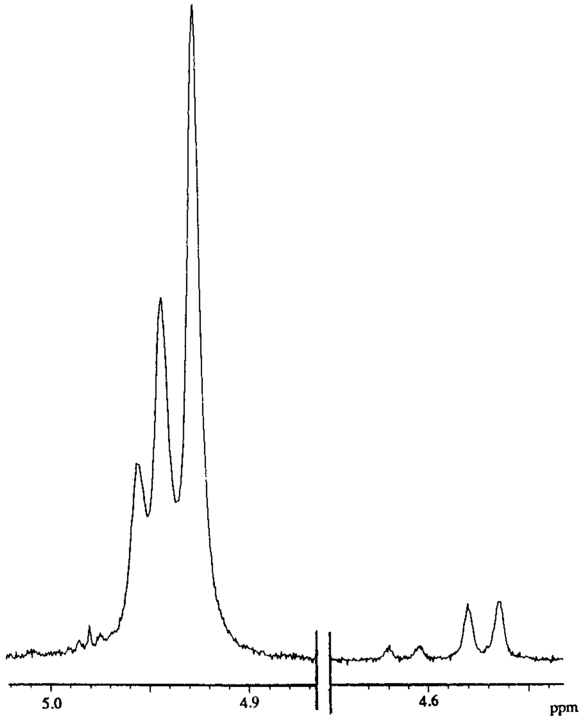

Figure 2. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **8** in the region of 4.5–5.1 ppm.

^{13}C{^{1}H} NMR spectroscopy was also found to be useful but less so than ^{1}H NMR for the characterization of these products. This is in part due to the limited sensitivity of the ^{13}C nucleus, which cannot distinguish the subtle changes of the chemical environment in the

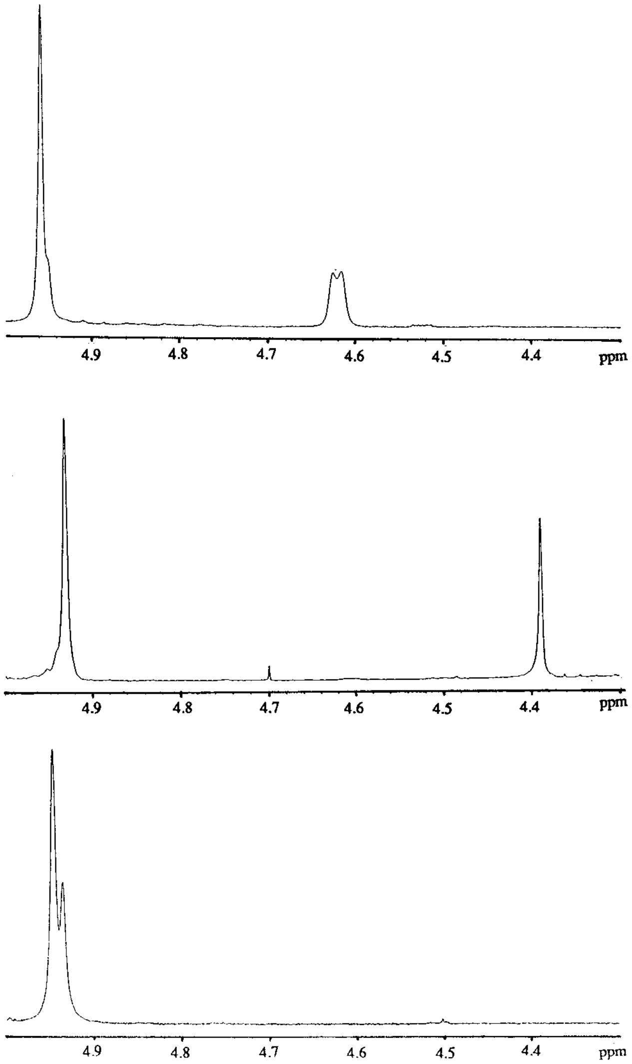

Figure 3. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) for **4**, **5**, and **12** (from top to bottom) in the region of 4.3−5.0 ppm.

dendritic structures. Nevertheless, in the case of the first- and second-generation dendrimers, the complete assignments of ^{13}C NMR spectra were possible. For example, Figure 4 shows the 100 MHz $^{13}C\{^1H\}$ NMR spectrum of **4**. The different "layers" of aromatic carbons give separate resonances in the region of δ 100−180 ppm. Figure 5 shows $^{13}C\{^1H\}$ NMR spectra in the region corresponding to the benzyl CH_2 for **4**, **5**, and **12**. The resonances due to the focal CH_2 groups are clearly distinguishable from the various functional groups, such as CH_2OH (δ 65 ppm) and CH_2Br (δ 34 ppm).

Thermal Properties. Differential scanning calorimetry (DSC) was employed to obtain the glass transition temperatures (T_g) of these dendrimers. The DSC traces were recorded in the temperature range of −10 to +110 °C. The data obtained and the calculated results are summarized in Table 2. It has been reported that the glass transition temperature of dendrimers is related to their chemical composition, chain-end functional groups, and molecular weights.[13] In the following text, we shall discuss these factors individually and compare our results with the reported data for the purely organic poly(benzyl phenyl ether) dendrimers. The difference between the reported poly(benzyl phenyl ether) dendrimers and the dendrimers prepared in this study is in the chain-end functional groups.

A plot of T_g against log molecular weight was obtained and is shown in Figure 6. The plot indicates that the T_g increases as the molecular weight of the dendrimer increases. The "leveling-off" effect is also observed in this study. It is interesting to note that in this case the T_g started leveling off at a molecular weight of about 3000, which is very similar to that observed for the poly(benzyl phenyl ether) dendrimers.[13] These results may imply that both types of dendrimers reach a densely-packed globular structure at a molecular weight above 3000 and also that the chain-end functional groups seem to have little effect on this characteristic property. For these ruthenium dendrimers, the T_g levels off at the molecular weight corresponding to the "third-generation dendritic wedges" (**6** or **7**), whereas in the case of the organic poly(benzyl phenyl ether) dendrimers, it corresponds to a "third-generation dendrimer".

According to eq 1, the $T_{g\infty}$ and K values can be obtained from a plot of T_g vs $[(n_e/M) - (n_e/M)_\infty]$ as shown in Figure 7.

$$T_g = T_{g\infty} - K[n_e/M - (n_e/M)_\infty] \qquad (1)$$

T_g, glass transition temperature;
$T_{g\infty}$, glass transition temperature at infinite
molecular weight; K, a constant, n_e, number
of the chain end functional groups; M,
molecular weight of dendrimer; $(n_e/M)_\infty$
a constant derived from linear regression
at infinite molecular weight

For the series of dendritic wedges with benzyl alcohol functional groups at the focal point, the n_e values were derived by making the assumption that the free volume of the chain-end functional group ($Cp(CO)_2RuCH_2CH_2CH_2O$) is much larger than that of the focal functional group ($PhCH_2OH$). The K values were then calculated from linear regression as the slope of the plot. Indeed, the K values obtained here (*ca.* 126 000) are significantly larger than those reported for the poly(benzyl phenyl ether) dendrimers with benzyl groups at the chain-ends (ca. 13 600).[13] Since the K values are proportionally related to the chain-end free volume (θ), therefore we were able to support the assumption made for the calculation of the K values. The K values obtained here for dendritic wedges and dendrimers are very different (126 000 and 208 000, respectively). We can ascribe this effect to the increase in the number of chain ends in the dendrimer series (3, 6, 12, 24, 48) which is significantly larger than that in the dendritic wedge series (2, 4, 8, 16). Also, since the same T_g value was obtained for both **6** and **7**, this suggests that the focal functional groups have very little effect on the T_g value.

The $T_{g\infty}$ values can be obtained from Figure 7 as the intercept of y axis. As expected, the $T_{g\infty}$ values for dendritic wedges and dendrimers are very similar (48 and 47 °C, respectively). Also, in a comparison of the $T_{g\infty}$ values between organic poly(benzyl phenyl ether) dendrimers (44 °C for dendritic wedges; 43 °C for dendrimers) and the ruthenium dendrimers, no significant difference in $T_{g\infty}$ value was found. This could be due to the fact that $T_{g\infty}$ values are largely dependent

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(13) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 1514.

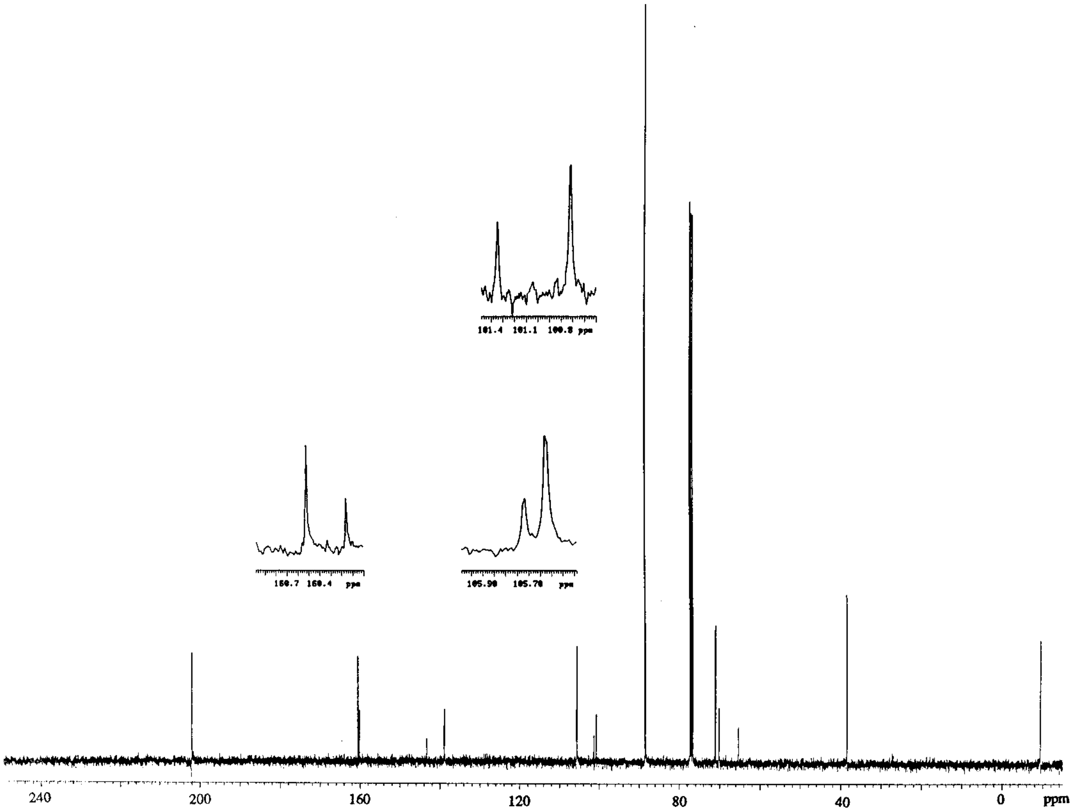

Figure 4. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of **4**.

on the polarity of chain-end functional groups rather than the size of them.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere using standard Schlenk tube techniques. Solvents were distilled from appropriate drying agents under nitrogen prior to use. Potassium carbonate was dried under vacuum (0.1 mmHg) at 90 °C overnight. All chemicals were obtained commercially, unless otherwise stated. $[CpRu(CO)_2\{(CH_2)_3Br\}]$[9] and 3,5-dihydroxybenzyl alcohol[14] were prepared by literature methods. Alumina (Merk, 90, active, neutral) was deactivated before use. The NMR spectra were recorded at ambient temperature in $CDCl_3$, at the following frequencies: ^1H, 399.952 MHz; ^{13}C, 100.577 MHz. The chemical shifts are reported relative to the residual signals of $CDCl_3$. The IR spectra were measured in CH_2Cl_2 solution. The differential scanning calorimetry (DSC) was carried out on the Perkin-Elmer PC series Model DSC7. For the determination of glass transition temperatures of the dendrimers, the sample was sealed hermetically in an aluminum pan and heated under nitrogen from −10 to +110 °C at a rate of 10 °C/min. For the crystalline solids **2** and **3**, before being submitted for DSC, the samples were heated at 110 °C for 5 min and then quenched in liquid nitrogen in order to freeze the samples to an amorphous state. The size-exclusion chromatography was performed on a Shimadzu liquid chromatography system consisting of a Shimadzu LC-6A pump and a Shimadzu SPD-6Av UV spectrophotometric detector (at 254 nm). THF at 40 °C with nominal flow rate of 1 mL/min was used as the mobil phase. The separations were achieved across banks of two Shodex columns (KF-804 and KF-806m). The system was calibrated versus commercially available monodispersed polystyrene standards.

General Procedure for Preparation of Benzyl Alcohol Dendritic Wedges. A mixture of the appropriate benzyl

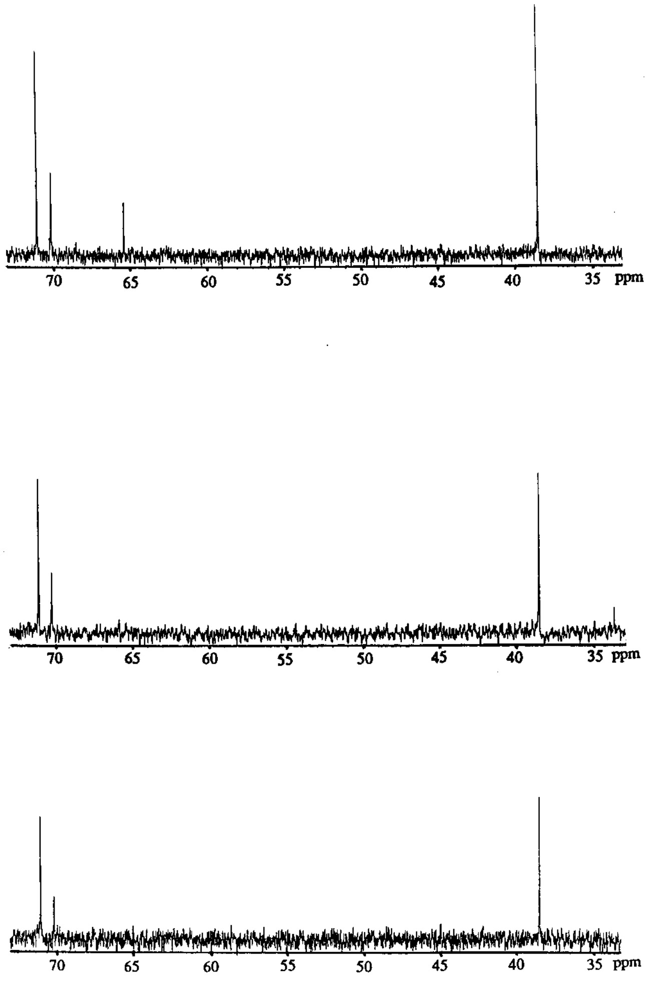

Figure 5. $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$, 100 MHz) for **4**, **5**, and **12** (from top to bottom) in the region of 33−73 ppm.

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[14] Pitt, C. G.; Seltzman, H. H.; Sayed, Y.; Twine, C. E., Jr.; Williams, D. L. *J. Org. Chem.* **1979**, *44*, 677.

Table 2. Thermal Data and Calculated Results for Selected Ruthenium Dendrimers

complexes	MW	T_g (°C)	log MW	n_e/M	$(n_e/M)_\infty$	$(n_e/M) - (n_e/M)_\infty$	$T_{g\infty}$ (°C)	K
2	666.66	−3	2.8239	0.003 000	0.002 595	0.000 405	48	126 000
4	1437.42	23	3.1576	0.002 783	0.002 595	0.000 188	48	126 000
6	2978.94	37	3.4741	0.002 686	0.002 595	0.000 091	48	126 000
7	3041.84	37	3.4831	0.002 630	0.002 595	0.000 035	48	126 000
8	6062.00	42	3.7826	0.002 639	0.002 595	0.000 044	48	126 000
11	2252.28	34	3.3526	0.002 664	0.002 595	0.000 069	47	208 000
13	9189.15	45	3.9633	0.002 609	0.002 595	0.000 014	47	208 000
14	18438.31	47	4.2657	0.002 603	0.002 595	0.000 008	47	208 000

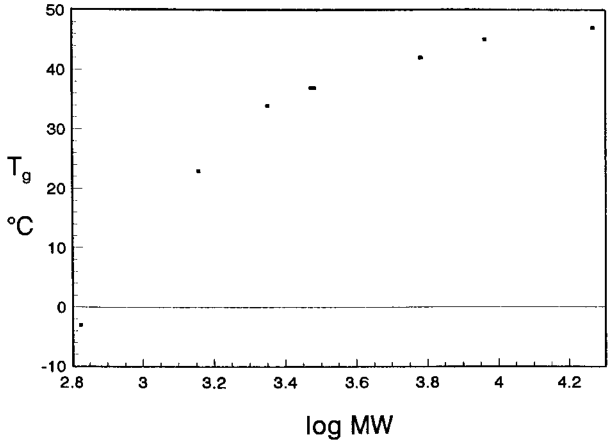

Figure 6. Plot of T_g vs log MW for selected ruthenium dendrimers.

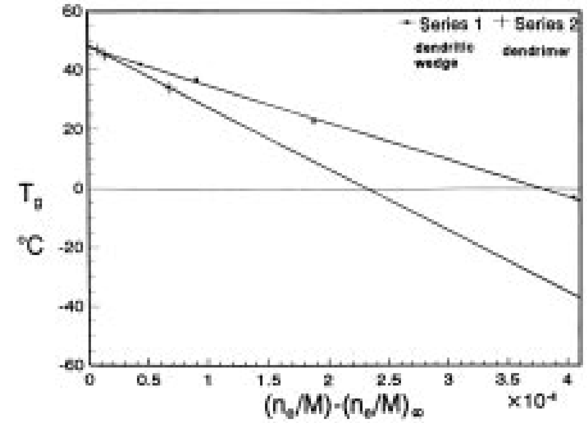

Figure 7. Plot of T_g vs $(n_e/M) - (n_e/M)_\infty$ for the dendritic wedges (series 1) and the dendrimers (series 2).

bromide dendritic wedge (2 equiv), 3,5-dihydroxybenzyl alcohol (1 equiv), potassium carbonate (3 equiv), and 18-crown-6 (0.2 equiv) in acetone (ca. 30 mL) was boiled under reflux and stirred vigorously for 48 h. The reaction was monitored by TLC, eluting with a 70% CH_2Cl_2/hexane solution. The solvent was removed under reduced pressure to give a yellow residue. This residue was then extracted with a 70% CH_2Cl_2/hexane solution. After filtration, the filtrate was concentrated and transferred to an alumina column. The polarity of the eluting solvent was gradually increased from 70% CH_2Cl_2/hexane to pure CH_2Cl_2. The purification procedure for each individual complex is outlined in the following text.

Complex 2. This was prepared from $[CpRu(CO)_2\{(CH_2)_3Br\}]$ and purified by column chromatography. A colorless band was collected, and the solvent was removed to give a colorless oil. The white crystalline product (70%) was obtained after recrystallization from an ether/hexane mixture at −15 °C: Mp 81−84 °C; IR ν 2012, 1948 cm^{-1}; ^1H NMR 6.49 (d, J(H,H) = 2 Hz, 2H, Ar), 6.38 (t, J(H,H) = 2 Hz, 1H, Ar), 5.25 (s, 10H, Cp), 4.61 (d, J(H,H) = 6 Hz, 2H, $ArCH_2$), 3.86 (t, J(H,H) = 7 Hz, 4H, CH_2OAr), 2.01 (m, 4H, CH_2), 1.69 (m, 4H, $RuCH_2$); ^{13}C NMR 202.09 (CO), 160.60, 143.14, 105.07, 100.51 (Ar), 88.54 (Cp), 71.05 (CH_2OAr), 65.53 ($ArCH_2$), 38.50 (CH_2), −9.33 ($RuCH_2$); MS (EI) m/z 638 ($M^+ - CO$). Anal. Found: C, 48.8; H, 4.3. Calcd for $C_{27}H_{28}O_7Ru_2$ (M_r = 666.66): C, 48.7; H, 4.2.

Complex 4. This was prepared from **3** and purified by column chromatography. The major colorless band was collected, and the solvent was removed to give a pale yellow oil. A colorless oil was then separated out from CH_2Cl_2/hexane at −15 °C. The final white rubbery product (70%) was obtained after drying the oil under high vacuum: IR ν 2012, 1948 cm^{-1}; ^1H NMR 6.61 (d, J(H,H) = 2 Hz, 2H, Ar), 6.55 (d, J(H,H) = 2 Hz, 5H, Ar), 6.41 (t, J(H,H) = 2 Hz, 2H, Ar), 5.25 (s, 20H, Cp), 4.96 (s, 4H, $ArCH_2$), 4.62 (d, J(H,H) = 4 Hz, 2H, CH_2OH), 3.86 (t, J(H,H) = 7 Hz, 8H, CH_2OAr), 2.01 (m, 8H, CH_2), 1.69 (m, 8H, $RuCH_2$); ^{13}C NMR 202.06 (CO), 160.52, 160.16, 143.31, 138.95, 105.72, 105.63, 101.35, 100.72 (Ar), 88.52 (Cp), 71.02 (CH_2OAr), 70.10 ($ArCH_2O$), 65.35 ($ArCH_2OH$), 38.46 (CH_2), −9.34 ($RuCH_2$); MS (FAB) m/z 1439 ($M^+ + 1$). Anal. Found: C, 51.1; H, 4.4. Calcd for $C_{61}H_{60}O_{15}Ru_4$ (M_r = 1437.42): C, 51.0; H, 4.2.

Complex 6. This was prepared from **5** and purified by column chromatography The major colorless band was collected, and the solvent was removed to give a pale yellow oil A colorless oil separated out from CH_2Cl_2/hexane at −15 °C A white glassy solid (74%) was obtained after drying the oil under high vacuum: IR ν 2012, 1948 cm^{-1}; ^1H NMR 6.64 (d, J(H,H) = 2 Hz, 2H, Ar), 6.59 (d, J(H,H) = 2 Hz, 4H, Ar), 6.53 (d br overlaping triplets, J(H,H) = 2 Hz, 11H, Ar), 6.38 (t, J(H,H) = 2 Hz, 4H, Ar), 5.23 (s, 40H, Cp), 4.96 (s, 4H, $ArCH_2O$), 4.95 (s, 8H, $ArCH_2O$), 4.62 (d, J(H,H) = 6 Hz, 2H, CH_2OH), 3.85 (t, J(H,H) = 7 Hz, 16H, CH_2O), 2.00 (m, 16H, CH_2), 1.69 (m, 16H, $RuCH_2$); ^{13}C NMR 202.10 (CO), 160.54, 160.16, 160.10, 138.94, 106.37, 105.69, 100.80 (Ar), 88.55 (Cp), 71.06, 70.18 (CH_2O), 38.47 (CH_2), −9.31 ($RuCH_2$); MS (FAB) m/z 2922 ($M^+ - 2CO$), Anal. Found: C, 51.4; H, 4.2. Calcd for $C_{129}H_{124}O_{31}Ru_8$ (M_r = 2979.09): C, 52.0; H, 4.2.

Complex 8. This was prepared from **7** and purified by column chromatography. The major colorless band was collected, and the solvent was removed to give a pale yellow oil. A colorless oil separated out from CH_2Cl_2/hexane at −15 °C. The final white glassy solid (66%) was obtained after drying the oil under high vacuum: IR ν 2012, 1948 cm^{-1}; ^1H NMR 6.66 (d, J(H,H) = 2 Hz, 2H, Ar), 6.59 (d, J(H,H) = 2 Hz, 12H, Ar), 6.53 (d br overlaping triplets, J(H,H) = 2 Hz, 23H, Ar), 6.38 (t, J(H,H) = 2 Hz, 8H, Ar), 5.21 (s, 80H, Cp), 4.96 (s, 4H, $ArCH_2O$), 4.94 (s, 8H, $ArCH_2O$), 4.93 (s, 16H, $ArCH_2O$), 4.57 (d, J(H,H) = 6 Hz, 2H, $ArCH_2OH$), 3.83 (t, J(H,H) = 6 Hz, 32H, CH_2O), 1.98 (m, 32H, CH_2), 1.67 (m, 32H, $RuCH_2$); ^{13}C NMR 202.13 (CO), 177.24, 160.54, 160.15, 160.10, 139.13, 138.92, 106.48, 106.46, 106.43, 105.71, 100.79 (Ar), 88.56 (Cp), 71.04, 70.17, 70.07 ($ArCH_2O$), 38.47 (CH_2), −9.37 ($RuCH_2$). Anal. Found: C, 52.7; H, 4.5. Calcd for $C_{265}H_{252}O_{63}Ru_{16}$ (M_r = 6062.00): C, 52.5; H, 4.2.

General Procedure for the Preparation of the Benzyl Bromide Dendritic Wedges. The appropriate benzyl alcohol dendritic wedge (1 equiv) with CBr_4 (1.25 equiv) was dissolved in the minimum volume of THF, followed by PPh_3 (1.25 equiv). The reaction mixture was stirred at room temperature and monitored by TLC (eluting with 30% CH_2Cl_2/hexane). For the later generation complexes, a large excess (up to 15 equiv) of CBr_4 and PPh_3 was required to drive the reactions to completion. This was achieved by adding PPh_3 and CBr_4 at a rate of

1.25 equiv every 10 min, until TLC showed that no more starting material was present. After the reaction was completed, distilled water (ca. 10 mL) was added to the reaction mixture, and the aqueous phase was extracted with CH_2Cl_2 (2 × 15 mL). The organic phase was then collected and dried over anhydrous $MgSO_4$. After filtration, CH_2Cl_2 was removed under reduced pressure to give a yellow oil. The crude product was purified by column chromatography, eluting with appropriate solvents. The purification details for each individual complex are given in the following text.

Complex 3. This was prepared from **2** and purified by column chromatography, eluting with a 30% CH_2Cl_2/hexane solution. The major colorless fraction was collected, and the solution was concentrated and cooled to −15 °C to give a white crystalline solid (65%): Mp 107−109 °C; IR *ν* 2012, 1948 cm^{-1}; ^{1}H NMR 6.45 (d, *J*(H,H) = 2 Hz, 2H, Ar), 6.31 (t, *J*(H,H) = 2 Hz, 1H, Ar), 5.19 (s, 10H, Cp), 4.34 (s, 2H, CH_2Br), 3.79 (t, *J*(H,H) = 7 Hz, 4H, CH_2O), 1.95 (m, 4H, CH_2), 1.61 (m, 4H, $RuCH_2$); ^{13}C NMR 202.05 (CO), 160.47, 139.45, 107.44, 101.42 (Ar), 88.53 (Cp), 71.09 (CH_2O), 38.44 (CH_2), 33.89 (CH_2Br), −9.39 ($RuCH_2$); MS (FAB) *m/z* 731 (M$^+$ + 1). Anal. Found: C, 43.9; H, 3.6; Br, 11.7. Calcd for $C_{27}H_{27}O_6BrRu_2$ (M_r = 729.55): C, 44.4; H, 3.7; Br, 11.0.

Complex 5. This was prepared from **4** and purified by column chromatography. The polarity of the eluting solvent was gradually increased from 30% CH_2Cl_2/hexane to 50% CH_2Cl_2/hexane. The major colorless fraction was collected, concentrated, and cooled to −15 °C. A colorless oil separated out, and a white rubbery solid was obtained after drying the oil under high vacuum: IR *ν* 2012, 1948 cm^{-1}; ^{1}H NMR 6.55 (d, *J*(H,H) = 2 Hz, 2H, Ar), 6.47 (d, *J*(H,H) = 2 Hz, 5H, Ar), 6.34 (t, *J*(H,H) = 2 Hz, 2H, Ar), 5.18 (s, 20H, Cp), 4.88 (s, 4H, $ArCH_2O$), 4.34 (s, 2H, CH_2Br), 3.80 (t, *J*(H,H) = 7 Hz, 8H, CH_2OAr), 1.94 (m, 8H, CH_2), 1.63 (m, 8H, $RuCH_2$); ^{13}C NMR 202.08 (CO), 160.57, 160.06, 139.66, 138.74, 108.16, 105.69, 102.24, 100.82 (Ar), 88.55 (Cp), 71.06 (CH_2OAr), 70.22 ($ArCH_2O$), 38.47 (CH_2), 33.66 (CH_2Br), −9.32 ($RuCH_2$); MS (FAB) *m/z* 1445 (M$^+$ − 2CO). Anal. Found: C, 48.3; H, 4.0; Br, 5.2. Calcd for $C_{61}H_{59}O_{14}BrRu_4$ (M_r = 1500.32): C, 48.8; H, 4.0; Br, 5.3.

Complex 7. This was prepared from **6** and purified by column chromatography. The polarity of the eluting solvent was gradually increased from 50% CH_2Cl_2/hexane to 70% CH_2Cl_2/hexane. The major colorless fraction was collected and concentrated. A pale yellow oil separated out from the solution at −15 °C, and a white glassy solid (73%) was obtained after drying the oil under high vacuum: IR *ν* 2012, 1948 cm^{-1}; ^{1}H NMR 6.66 (d, *J*(H,H) = 2 Hz, 4H, Ar), 6.62 (d, *J*(H,H) = 2 Hz, 2H, Ar), 6.57 (t, *J*(H,H) = 2 Hz, 3H, Ar), 6.55 (d, *J*(H,H) = 2 Hz, 8H, Ar), 6.40 (t, *J*(H,H) = 2 Hz, 4H, Ar), 5.23 (s, 40H, Cp), 4.96 (s, 12H, $ArCH_2O$), 4.41 (s, 2H, CH_2Br), 3.86 (t, *J*(H,H) = 7 Hz, 16H, CH_2O), 2.01 (m, 16H, CH_2), 1.69 (m, 16H, $RuCH_2$); ^{13}C NMR 202.10 (CO), 160.56, 160.18, 138.92 106.46, 105.70, 100.80 (Ar), 88.55 (Cp), 71.05 (CH_2O), 70.21, 70.11 ($ArCH_2O$), 38.48 (CH_2), −9.30 ($RuCH_2$); MS (FAB) *m/z* 2988 (M$^+$ − 2CO). Anal. Found: C, 50.5; H, 4.4. Calcd for $C_{129}H_{123}O_{30}BrRu_8$ (M_r = 3041.84): C, 50.8; H, 4.1.

Complex 9. This was prepared from **8** and purified by column chromatography, eluting with a 50% CH_2Cl_2/hexane solution. The major colorless band was collected and concentrated. A pale yellow oil separated out from the solution at −15 °C, and the final white glassy solid (66%) was obtained after drying the oil under high vacuum: IR *ν* 2012, 1948 cm^{-1}; ^{1}H NMR 6.67 (d, *J*(H,H) = 2 Hz, 8H, Ar), 6.63 (d, *J*(H,H) = 2 Hz, 4H, Ar), 6.54 (d, *J*(H,H) = 2 Hz, 25H, Ar), 6.40 (t, *J*(H,H) = 2 Hz, 8H, Ar), 5.22 (s, 80H, Cp), 4.96, 4.94 (s, 30H, $ArCH_2O$), 4.38 (s, 2H, CH_2Br), 3.85 (t, *J*(H,H) = 7 Hz, 32H, CH_2O), 2.00 (m, 32H, CH_2), 1.68 (m, 32H, $RuCH_2$); ^{13}C NMR 202.11 (CO), 160.54, 160.16, 139.08, 138.92, 106.49, 105.70, 100.79 (Ar), 88.55 (Cp), 71.02 (CH_2O), 70.16, 70.07 ($ArCH_2O$), 38.46 (CH_2), −9.30 ($RuCH_2$). Anal. Found: C, 52.1; H, 4.2. Calcd for $C_{265}H_{251}O_{62}BrRu_{16}$ (M_r = 6124.89): C, 52.0; H, 4.1.

General Procedure for the Preparation of Dendrimers. A mixture of the appropriate benzyl bromide dendritic wedge (3 equiv), 1,1,1-tris(4′-hydroxyphenyl)ethane (1 equiv), potassium carbonate (5 equiv), and 18-crown-6 (0.3 equiv) in acetone (ca. 30 mL) was heated at reflux and stirred vigorously for 48 h. The reaction was monitored by TLC, eluting with a 60% CH_2Cl_2/hexane solution. The solvent was removed to give a pale yellow residue. The residue was then extracted with a 70% CH_2Cl_2/hexane solution. After filtration, the filtrate was concentrated and transferred to an alumina column. The purification procedure for each individual complex is outlined in the following text.

Complex 10. This was prepared from [CpRu(CO)$_2${(CH$_2$)$_3$Br}] and purified by column chromatography, eluting with a 50% CH_2Cl_2/hexane solution. The colorless band was collected and concentrated. A pale yellow oil separated out from the solution at −15 °C, and the final white glassy solid (32%) was obtained after drying the oil under high vacuum: IR *ν* 2012, 1948 cm^{-1}; ^{1}H NMR 6.92 (d, *J*(H,H) = 9 Hz, 6H, $\mathrm{Ar^{CORE}}$), 6.71 (d, *J*(H,H) = 9 Hz, 6H, $\mathrm{Ar^{CORE}}$), 5.19 (s, 15H, Cp), 3.79 (t, *J*(H,H) = 7 Hz, 6H, CH_2O), 2.04 (m, 9H, CH_2 + CH_3), 1.68 (m, 6H, $RuCH_2$); ^{13}C NMR 202.07 (CO), 157.11, 141.63, 129.57, 113.59 ($\mathrm{Ar^{CORE}}$), 88.53 (Cp), 70.94 (CH_2O), 50.55 (*C*CH3), 38.59 (CH_2), 30.77 (C*C*H3), −9.02 ($RuCH_2$); MS (FAB) *m/z* 1097 (M$^+$ + 1). Anal. Found: C, 55.1; H, 4.2. Calcd for $C_{50}H_{48}O_9Ru_3$ (M_r = 1096.14): C, 54.8; H, 4.4.

Complex 11. This was prepared from **3** and purified by column chromatography, eluting with a 50% CH_2Cl_2/hexane solution. The major colorless fraction was collected and concentrated. A pale yellow oil separated out from the solution at −15 °C, and the final white glassy solid (70%) was obtained after drying the oil under high vacuum: IR *ν* 2012, 1948 cm^{-1}; ^{1}H NMR 6.98 (d, *J*(H,H) = 9 Hz, 6H, $\mathrm{Ar^{CORE}}$), 6.85 (d, *J*(H,H) = 9 Hz, 6H, $\mathrm{Ar^{CORE}}$), 6.56 (d, *J*(H,H) = 2 Hz, 6H, Ar), 6.40 (t, *J*(H,H) = 2 Hz, 3H, Ar), 5.25 (s, 30H, Cp), 4.96 (s, 6H, $ArCH_2O$), 3.86 (t, *J*(H,H) = 7 Hz, 12H, CH_2O), 2.10 (s, 3H, CH_3), 2.01 (m, 12H, CH_2), 1.69 (m, 12H, $RuCH_2$); ^{13}C NMR 202.10 (CO), 160.54, 139.33, 105.69, 100.71 (Ar), 156.87, 142.01, 129.63, 114.02 ($\mathrm{Ar^{CORE}}$), 88.56 (Cp), 71.05 (CH_2O), 70.11 ($ArCH_2O$), 50.66 (*C*CH$_3$), 38.49 (CH_2), 30.10 (C*C*H$_3$), −9.31 ($RuCH_2$); MS (FAB) *m/z* 2192 (M$^+$ − 60). Anal. Found: C, 54.15; H, 4.4. Calcd for $C_{101}H_{96}O_{21}Ru_6$ (M_r = 2252.28): C, 53.9; H, 4.3.

Complex 12. This was prepared from **5** and purified by column chromatography. The polarity of the eluting solvent was gradually increased from 50% CH_2Cl_2/hexane to 70% CH_2Cl_2/hexane. The major colorless fraction was collected and concentrated. A pale yellow oil separated out from the solution at −15 °C, and the white glassy solid (76%) was obtained after drying the oil under high vacuum: IR *ν* 2012, 1948 cm^{-1}; ^{1}H NMR 7.01 (d, *J*(H,H) = 9 Hz, 6H, $\mathrm{Ar^{CORE}}$), 6.86 (d, *J*(H,H) = 9 Hz, 6H, $\mathrm{Ar^{CORE}}$), 6.67 (d, *J*(H,H) = 2 Hz, 6H, Ar), 6.55 (d, *J*(H,H) = 2 Hz, 15H, Ar), 6.40 (t, *J*(H,H) = 2 Hz, 6H, Ar), 5.22 (s, 60H, Cp), 4.95 (s, 12H, $ArCH_2O$), 4.94 (s, 18H, $ArCH_2O$), 3.86 (t, *J*(H,H) = 7 Hz, 24H, CH_2O), 2.11 (s, 3H, CCH_3), 2.01 (m, 24H, CH_2), 1.68 (s, 24H, $RuCH_2$); ^{13}C NMR 202.11 (CO), 160.55, 160.14, 138.93, 129.67, 114.01, 106.51, 106.49, 105.71, 100.79 (Ar + $\mathrm{Ar^{CORE}}$), 88.55 (Cp), 71.04 (CH_2O), 70.18 ($ArCH_2O$), 38.47 (CH_2), −9.31 ($RuCH_2$); MS (FAB) *m/z* 4509 (M$^+$ − 2CO). Anal. Found: C, 53.3; H, 4.0. Calcd for $C_{203}H_{192}O_{45}Ru_{12}$ (M_r = 4564.57): C, 53.4; H, 4.2.

Complex 13. This was prepared from **7** and purified by column chromatography, eluting with a 60% CH_2Cl_2/hexane solution. The major colorless fraction was collected and concentrated. A pale yellow oil separated out from solution at −15 °C, and the final white glassy solid (54%) was obtained after drying the oil under high vacuum: IR *ν* 2012, 1948 cm^{-1}; ^{1}H NMR 7.01 (d, *J*(H,H) = 9 Hz, 6H, $\mathrm{Ar^{CORE}}$), 6.87 (d, *J*(H,H) = 9 Hz, 6H, $\mathrm{Ar^{CORE}}$), 6.69 (d, *J*(H,H) = 2 Hz, 6H, Ar), 6.67 (d, *J*(H,H) = 2 Hz, 12H, Ar), 6.54 (d, *J*(H,H) = 2 Hz, 33H, Ar), 6.39 (t, *J*(H,H) = 2 Hz, 12H, Ar), 5.21 (s, 120H, Cp), 4.94 (s, 42H, $ArCH_2O$), 3.84 (t, *J*(H,H) = 7 Hz, 48H, CH_2O), 2.04 (s, 3H, CCH_3), 1.99 (m, 48H, CH_2), 1.67 (m, 48H, $RuCH_2$); ^{13}C NMR 202.13 (CO), 160.54, 160.16, 139.09, 138.92, 106.53, 105.70, 100.79 (Ar + Ar^{CORE}), 88.56 (Cp), 71.03, 70.17 ($ArCH_2O$), 38.47 (CH_2), −9.30 ($RuCH_2$). Anal. Found: C, 53.3; H, 4.4. Calcd for $C_{407}H_{384}O_{93}Ru_{24}$ (M_r = 9189.15): C, 53.2; H, 4.2.

Preparation of 14. A mixture of **9** (110 mg, 0.018 mmol), 1,1,1-tris(4-hydroxyphenyl)ethane (1.8 mg, 0.0058 mmol), potassium carbonate (320 mg, 2.3 mmol, excess), and 18-crown-6 (49 mg, 0.18 mmol) in acetone (30 mL) was stirred vigorously and heated at reflux for 48 h. The reaction was monitored by TLC; however, no change was observed. After 48 h, another portion of 1,1,1-tris(4-hydroxyphenyl)ethane (22 mg, 0.072 mmol) was added into the reaction, and the reaction mixture was stirred and heated at reflux for another 24 h. The solvent was then removed under reduced pressure to give a pale yellow residue. The residue was extracted with CH_2Cl_2 (*ca.* 20 mL), and the white precipitate was filtered off. The pale yellow filtrate was concentrated and transferred to an alumina column, eluting with a 60% CH_2Cl_2/hexane solution. The major colorless fraction was collected and concentrated. A pale yellow oil was separated out from the solution at −15 °C, and the final white glassy solid (70 mg, 66%) was obtained after drying this oil under high vacuum: IR ν 2012, 1948 cm^{-1}; ^1H NMR 7.01 (br d, 6H, Ar^{CORE}), 6.84 (br d, 6H, Ar^{CORE}), 6.65 (br, 42H, Ar), 6.52 (br, 69H, Ar), 6.37 (br, 24H, Ar), 5.17 (s, 240H, Cp), 4.91 (br, 90H, $ArCH_2O$), 3.82 (br, 96H, CH_2O), 1.96 (m, 99H, CH_2 + CH_3), 1.66 (m, 96H, $RuCH_2$); ^{13}C NMR 202.13 (CO), 160.53, 160.13, 138.93, 106.51, 105.70, 101.63, 100.80 (Ar + Ar^{CORE}), 88.56 (Cp), 71.03, 70.17 ($ArCH_2O$), 38.47 (CH_2), −9.29 ($RuCH_2$). Anal. Found: C, 52.9; H, 4.3. Calcd for $C_{815}H_{768}O_{189}Ru_{48}$ (M_r = 18438.31): C, 53.1; H, 4.2.

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