

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/207018852>

Polyanionic Carbosilane and Carbosiloxane Metallodendrimers Based on Cobaltabisdicarbollide Derivatives

ARTICLE *in* ORGANOMETALLICS · SEPTEMBER 2009

Impact Factor: 4.13 · DOI: 10.1021/om9005643

CITATIONS

26

READS

21

4 AUTHORS, INCLUDING:



Emilio José Juárez-Pérez

Okinawa Institute of Science and Technology

41 PUBLICATIONS 900 CITATIONS

SEE PROFILE



Clara Viñas

Materials Science Institute of Barcelona

348 PUBLICATIONS 5,512 CITATIONS

SEE PROFILE



Rosario Núñez

Spanish National Research Council

88 PUBLICATIONS 1,516 CITATIONS

SEE PROFILE

Polyanionic Carbosilane and Carbosiloxane Metallodendrimers Based on Cobaltabisdicarbollide Derivatives

Emilio José Juárez-Pérez, Clara Viñas, Francesc Teixidor, and Rosario Núñez*

Institut de Ciència de Materials, CSIC, Campus U.A.B., 08193 Bellaterra, Spain

Received July 1, 2009

Carbosilane and carbosiloxane metallodendrimers that contain one, four, and eight peripheral cobaltabisdicarbollide derivatives have been synthesized using regiospecific hydrosilylation of vinyl-terminated dendrimers with Cs[1,1'- μ -SiMeH-3,3'-Co(1,2-C₂B₉H₁₀)₂], **1**. A methodology to synthesize a trifunctional molecule containing one cobaltabisdicarbollide and three vinylsilane moieties, **2**, has been developed starting with tetravinylsilane. The first- and second-generation of anionic metallacarborane-containing metallodendrimers, **3**, **4**, and **5**, were constructed via hydrosilylation of carbosilane dendrimers functionalized with four or eight vinyl functions, by using **1** as the hydrosilylation agent. Furthermore, it has been possible to apply this methodology to vinyl-terminated cyclocarbosiloxane dendrimers to yield metallodendrimers, **6**, **7**, and **8**, which contain four (**6**) and eight (**7**, **8**) peripheral cobaltabisdicarbollide units. Products are fully characterized by FTIR, NMR, and UV-vis spectroscopies. For metallodendrimers, the UV-vis absorptions have been a good tool for estimating the experimental number of cobaltabisdicarbollide moieties attached to the periphery and consequently to corroborate the good level of functionalization of the dendrimers. In addition, UV-vis spectroscopic measurements have also allowed the study of the solubility and behavior in water/DMSO solutions of these metallodendrimers.

Introduction

Dendrimers are known for their well-defined globular hyperbranched structures and low polydispersity. These properties combined with the high number of functional groups and metal fragments, localized at the core or at the periphery, provide a wide range of macromolecules with interesting catalytic, redox, magnetic, photo-optical, and biomedical properties.^{1,2} In the past few years, carbosilane

dendrimers³ have been used as inert scaffolds for attaching functional groups on the periphery according to the required application.^{4,5} More recently, examples of cationic carbosilane dendrimers have been described to be used as potential carriers for phosphorothioate oligodeoxynucleotide (ODN)⁶ or for other biocompatible applications.⁷ However, to our knowledge, few reports exist on anionic silyl-containing

*Corresponding author. Tel: +34 93 580 1853. Fax: +34 93 580 5729. E-mail: rosario@icmab.es.

(1) (a) *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M., Tomalia, D. A., Eds.; Wiley Series in Polymer Science; John Wiley & Sons, Ltd.: UK, 2001. (b) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, 101, 2991. (c) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, 34, 181. (d) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Synthesis, Applications*; Wiley: New York, 2002. (e) Boas, U.; Heegarard, P. M. H. *Chem. Soc. Rev.* **2004**, 33, 43. (f) Caminade, A. M.; Majoral, J. P. *Acc. Chem. Res.* **2004**, 37, 341. (g) Liang, C.; Fréchet, J. M. *Prog. Polym. Sci.* **2005**, 30, 385. (h) Jiang, D. L.; Aida, T. *Prog. Polym. Sci.* **2005**, 30, 403. (i) Astruc, D.; Ornelas, C.; Ruiz, J. *Acc. Chem. Res.* **2008**, 41, 841. (j) Caminade, A. M.; Servin, P.; Laurent, R.; Majoral, J. P. *Chem. Soc. Rev.* **2008**, 37, 56.

(2) (a) Qualmann, B.; Kessels, M. M.; Mussiol, H.-J.; Sierralta, W. D.; Jungblut, P. W.; Moroder, L. *Angew. Chem.* **1996**, 108, 970. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 909. (b) Yamamoto, K.; Higuchi, M.; Shiki, S.; Tsuruta, M.; Chiba, H. *Nature* **2002**, 415, 509. (c) Frey, H.; Haag, R. *Rev. Mol. Biotechnol.* **2002**, 90, 257. (d) van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Rev.* **2002**, 102, 3717. (e) Gillies, E. R.; Fréchet, J. M. J. *Drug. Discovery Today* **2005**, 10, 35. (f) Méry, D.; Astruc, D. *Coord. Chem. Rev.* **2006**, 250, 1965. (g) Cheng, Y.; Wang, J.; Rao, T.; He, X.; Xu, T. *Front. Biosci.* **2008**, 13, 1447. (h) Cheng, Y.; Xu, Z.; Ma, M.; Xu, T. *J. Pharm. Sci.* **2008**, 97, 123. (i) Agarwal, A.; Saraf, S.; Asthana, A.; Gupta, U.; Gajbhiye, V.; Jain, N. K. *Int. J. Pharm.* **2008**, 350, 3. (j) Caminade, A. M.; Turrin, C. O.; Majoral, J. P. *Chem.—Eur. J.* **2008**, 14, 7422. (k) Jang, W. D.; Selim, K. M. K.; Lee, C. H.; Kang, I. K. *Prog. Polym. Sci.* **2009**, 34, 1, and references therein.

(3) (a) van der Made, A. W.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400. (b) Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrader, R. L. *Organometallics* **1994**, 13, 2682. (c) Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. J. *Chem. Soc., Chem. Commun.* **1994**, 2575. (d) van der Made, A. W.; van Leeuwen, P. W. N. M.; de Wilde, J. C.; Brances, R. A. *C. Adv. Mater.* **1993**, 5, 466. (e) Zhan, L.-L.; Roovers, J. *Macromolecules* **1993**, 26, 963. (f) Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1995**, 14, 5362. (g) Krsda, S. W.; Seyferth, D. *J. Am. Chem. Soc.* **1998**, 120, 3604. (h) Lühmann, B.; Lang, H.; Bröning, K. *Phosphorus Sulfur Silicon Relat. Elem.* **2001**, 65, 133. (i) Casado, M. A.; Hack, V.; Camerano, J. A.; Ciriano, M. A.; Tejel, C.; Oro, L. A. *Inorg. Chem.* **2005**, 44, 9122. (j) Donnio, B.; Buathong, S.; Bury, I.; Guillon, D. *Chem. Soc. Rev.* **2007**, 36, 1945. (k) Zamora, M.; Alonso, B.; Pastor, C.; Cuadrado, I. *Organometallics* **2007**, 26, 5153. (l) Andrés, R.; de Jesús, E.; Flores, J. C. *New J. Chem.* **2007**, 31, 1161. (m) Kim, C.; An, K. *J. Organomet. Chem.* **1997**, 547, 55. (n) Kim, C.; An, K. *Bull. Korean Chem. Soc.* **1997**, 18, 164. (o) Kim, C.; Park, E.; Kang, E. *Korean Chem. Soc.* **1996**, 40, 347.

(4) (a) Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Losada, J. *Coord. Chem. Rev.* **1999**, 193–195, 395. (b) Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 1951. (c) Frey, H.; Schlenk, C. *Top. Curr. Chem.* **2000**, 210, 69. (d) Kreiter, R.; Kleij, A. W.; Gebbink, R. J. M. K.; van Koten, G. *Top. Curr. Chem.* **2001**, 217, 163.

(5) (a) Kleij, A. W.; Gossage, R. A.; Gebbink, R. J. M. K.; Brinkmann, N.; Reijerse, E. J.; Kragl, U.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2000**, 122, 12112. (b) Rossell, O.; Seco, M.; Angurell, I. *C. R. Chim.* **2003**, 6, 803. (c) Angurell, I.; Rossell, O.; Seco, M.; Ruiz, E. *Organometallics* **2005**, 24, 6365. (d) Rodríguez, L. I.; Rossell, O.; Seco, M.; Grabulosa, A.; Muller, G.; Rocamora, M. *Organometallics* **2006**, 25, 1368. (e) *Silicon-Containing Dendritic Polymers (Advances in Silicon Science)*; Dvornic, P.; Owen, M. J., Eds.; Springer, 2009; Vol. 2.

dendrimers designed to have a surface of negative charges that could be capable of specific binding to several different cationic species.^{31,8} During our research on high boron-content molecules,⁹ we recently developed different synthetic strategies for the preparation of anionic carboranyl-terminated dendrimeric systems, by using carbosilane dendrimers as a scaffold in which *nido*-carborane clusters were placed at the periphery.¹⁰ Following our studies on developing boron-rich anionic dendrimers, we considered it appropriate to use a derivative of the monoanionic cobaltabisdicarbollide, $[(3,3'\text{-Co-(1,2-C}_2\text{B}_9\text{H}_{11})_2)]^-$,¹¹ to be peripherally attached to the dendrimers. This metallacarborane is an electron-deficient sandwich with 18 boron atoms that is characterized by its extraordinary chemical and thermal stability.^{11b} This compound is hydrophobic¹² and a low nucleophilic anion,^{13,14}

which has made it suitable for a wide range of applications,¹⁵ such as the extraction of radionuclides,¹⁶ in conducting organic polymers,¹⁷ in ion-selective PVC membrane electrodes for tuberculosis drug analysis,¹⁸ or for its use in medicine.¹⁹ For this purpose, bioactive functionalized metallacarboranes have been characterized,²⁰ and cobaltabisdicarbollide derivatives have been attached to different organic groups and biomolecules.^{21,22} Up to today, the usual method to attach this metallacarborane to the different groups has been through the boron atom in position 8', by the reaction of the dioxane-metallacarborane derivative $[8\text{-O}(\text{CH}_2\text{CH}_2)_2\text{O-3',3'-Co(1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^{23}$ with the corresponding nucleophiles.^{20–22,24} Here, we report the preparation of boron-rich polyanionic macromolecules by using a new approach to bind metallacarboranes to carbosilane and carbosiloxane dendrimers via hydrosilylation reactions²⁵ of vinyl-terminated dendrimers with the recently reported C_c-silyl-substituted cobaltabisdicarbollide derivative $\text{Cs}[1,1'\text{-}\mu\text{-SiMeH-3,3'-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]$, **1**.²⁶ In addition, a solubility test of the dendrimers in DMSO/water has been carried out using the UV–visible spectroscopy.

Results and Discussion

Synthesis of Carbosilane and Carbosiloxane Metallodendrimers. With the objective to design and prepare polyanionic carbosilane and carbosiloxane dendrimers peripherally decorated with metallacarboranes, suitable dendritic molecules containing terminal C=C functionalities were prepared according to the literature.³ The 1,3,5,7-tetramethylvinylcyclotetrasiloxane (TMViCTS), as core molecule (generation 0), the carbosilane dendrimers 1G-Vi₄, 1G-Vi₈, and 2G-Vi₈, and

(6) (a) Ortega, P.; Bermejo, J. F.; Chonco, L.; de Jesús, E.; de la Mata, F. J.; Fernández, G.; Flores, J. C.; Gómez, R.; Serramia, M. J.; Muñoz-Fernández, M. A. *Eur. J. Inorg. Chem.* **2006**, 7, 1388. (b) Bermejo, J. F.; Ortega, P.; Chonco, L.; Eritja, R.; Samaniego, R.; Müller, M.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R.; Muñoz-Fernández, M. A. *Chem.—Eur. J.* **2007**, 13, 483. (c) Chonco, L.; Bermejo-Martín, J. F.; Ortega, P.; Shcharbin, D.; Pedziwiatr, E.; Klajnert, B.; M.; de la Mata, F. J.; Gómez, R.; Bryszewska, M.; Muñoz-Fernández, M. A. *Org. Biomol. Chem.* **2007**, 5, 1886. (d) Gras, R.; Almonacid, L. S.; Ortega, P.; Serramia, M. J.; Gómez, R.; de la Mata, F. J.; López-Fernández, L. A.; Muñoz-Fernández, M. A. *Pharm. Res.* **2009**, 26, 577.

(7) (a) Kleij, A. W.; van de Coevering, R.; Klein-Gebbink, R. J. M.; Nordman, A.-M.; Spek, A. L.; van Koten, G. *Chem.—Eur. J.* **2001**, 7, 181. (b) Weber, N.; Ortega, P.; Clemente, M. I.; Shcharbin, D.; Bryszewska, M.; de la Mata, F. J.; Gómez, R.; Muñoz-Fernández, M. A. *J. Controlled Release* **2008**, 132, 2008.

(8) (a) Ornelas, C.; Boisselier, E.; Martinez, V.; Pianet, I.; Ruiz-Arenzaes, J.; Astruc, D. *Chem. Commun.* **2007**, 5093. (b) Boisselier, E.; Ornelas, C.; Pianet, I.; Ruiz-Arenzaes, J.; Astruc, D. *Chem.—Eur. J.* **2008**, 14, 5577. (c) Malik, N.; Wiwattanapatee, R.; Klopsch, R.; Lorenz, K.; Frey, H.; Weener, J. W.; Meijer, E. W.; Paulus, W.; Duncan, R. *J. Controlled Release* **2000**, 65, 133.

(9) (a) Núñez, R.; González, A.; Viñas, C.; Teixidor, F.; Sillanpää, R.; Kivekäs, R. *Org. Lett.* **2005**, 7, 231. (b) Núñez, R.; González-Campo, A.; Viñas, C.; Teixidor, F.; Sillanpää, R.; Kivekäs, R. *Organometallics* **2005**, 24, 6351. (c) Núñez, R.; González-Campo, A.; Laromaine, A.; Teixidor, F.; Sillanpää, R.; Kivekäs, R.; Viñas, C. *Org. Lett.* **2006**, 8, 4549. (d) Lerouge, F.; Vicas, C.; Teixidor, F.; Núñez, R.; Abreu, A.; Xochitiotzi, E.; Santillan, R.; Farfán, N. *Dalton Trans.* **2007**, 1898.

(10) (a) González-Campo, A.; Viñas, C.; Teixidor, F.; Núñez, R.; Kivekäs, R.; Sillanpää, R. *Macromolecules* **2007**, 40, 5644. (b) González-Campo, A.; Juárez-Pérez, E. J.; Viñas, C.; Boury, B.; Kivekäs, R.; Sillanpää, R.; Núñez, R. *Macromolecules* **2008**, 41, 8458.

(11) (a) Hawthorne, M. F.; Andrews, T. D. *J. Chem. Soc., Chem. Commun.* **1965**, 443. (b) Sivaev, I. B.; Bregadze, V. I. *Collect. Czech. Chem. Commun.* **1999**, 64, 783.

(12) (a) Ma, L.; Hamdi, J.; Hawthorne, M. F. *Inorg. Chem.* **2005**, 44, 7249. (b) Matejcek, P.; Cigler, P.; Procházka, K.; Kral, V. *Langmuir* **2006**, 22, 575. (c) Chevrot, G.; Schurhammer, R.; Wipff, G. *J. Phys. Chem. B* **2006**, 110, 9488.

(13) (a) Strauss, S. H. *Chem. Rev.* **1993**, 93, 927. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, 31, 133.

(14) Masalles, C.; Llop, J.; Viñas, C.; Teixidor, F. *Adv. Mater.* **2002**, 14, 826.

(15) Plešek, J. *Chem. Rev.* **1992**, 92, 269.

(16) (a) Viñas, C.; Gómez, S.; Bertran, J.; Teixidor, F.; Dozol, J.-F.; Rouquette, H. *Chem. Commun.* **1998**, 191. (b) Viñas, C.; Gómez, S.; Bertran, J.; Teixidor, F.; Dozol, J.-F.; Rouquette, H. *Inorg. Chem.* **1998**, 37, 3640. (c) Grüner, B.; Plešek, J.; Baca, J.; Cisarova, I.; Dozol, J.-F.; Rouquette, H.; Viñas, C.; Selucky, P.; Rais, J. *New J. Chem.* **2002**, 26, 1519. (d) Mikulášek, L.; Grüner, B.; Crenguta, D.; Rudzevich, V.; Böhmer, V.; Haddaoui, J.; Hubscher-Bruder, V.; Arnaud-Nue, F.; Caslavsky, J.; Selucky, P. *Eur. J. Org. Chem.* **2007**, 4772.

(17) (a) Masalles, C.; Borrós, S.; Viñas, C.; Teixidor, F. *Adv. Mater.* **2000**, 12, 1199. (b) Borrós, S.; Llop, J.; Viñas, C.; Teixidor, F. *Adv. Mater.* **2002**, 14, 449. (c) Gentil, S.; Crespo, E.; Rojo, I.; Friang, A.; Viñas, C.; Teixidor, F.; Grüner, B.; Gabel, D. *Polymer* **2005**, 46, 12218. (d) Crespo, E.; Gentil, S.; Viñas, C.; Teixidor, F. *J. Phys. Chem. C* **2007**, 111, 18381. (e) Errachid, A.; Caballero, D.; Crespo, E.; Bessueille, F.; Pla-Roca, M.; Mills, C.; Christopher, A.; Teixidor, F.; Samitier, J. *Nanotechnology* **2007**, 18, 485301. (f) Stoica, A. I.; Viñas, C.; Teixidor, F. *Chem. Commun.* **2008**, 6492.

(18) Stoica, A. I.; Viñas, C.; Teixidor, F. *Chem. Commun.* **2008**, 48, 6492.

(19) (a) Hawthorne, M. F.; Maderna, A. *Chem. Rev.* **1999**, 99, 3421. (b) Hao, E.; Vicente, M. G. H. *Chem. Commun.* **2005**, 1306. (c) Barth, R. F.; Coderre, J. A.; Vicente, M. G. H.; Blue, T. E. *Clin. Cancer Res.* **2005**, 11, 3987. (d) Gottumukkala, V.; Ongayi, O.; Baker, D. G.; Lomax, L. G.; Vicente, M. G. H. *Bioorg. Med. Chem.* **2006**, 14, 1871. (e) Wang, J.-Q.; Ren, C.-X.; Weng, L.-H.; Jin, G.-X. *Chem. Commun.* **2006**, 162. (f) Bregadze, V. I.; Sivaev, I. B.; Glazun, S. A. *Anti-Cancer Agents Med. Chem.* **2006**, 6, 75. (f) Cigler, P.; Kozisek, M.; Rezacova, P.; Brynda, J.; Otwinowski, Z.; Pokorná, J.; Plešek, J.; Grüner, B.; Dolecková-Maresová, L.; Masa, M.; Sedláček, J.; Bodem, J.; Kräusslich, H.-G.; Král, V.; Konvalinka, J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, 102, 15394. (g) Crossley, E. L.; Ziolkowski, E. J.; Coderre, J. A.; Rendina, L. M. *Mini-Rev. Med. Chem.* **2007**, 7, 3003.

(20) Valliant, J. F.; Guenther, K. J.; King, A. S.; Morel, P.; Schaffer, O. O.; Sogbein, K. A.; Stephenson, K. A. *Coord. Chem. Rev.* **2002**, 232, 173.

(21) (a) Olejniczak, A. B.; Plešek, J.; Kriz, O.; Lesnikowski, Z. J. *Angew. Chem., Int. Ed.* **2003**, 42, 5720. (b) Lesnikowski, Z.; Paradowska, E.; Olejniczak, A. B.; Studzinska, M.; Seekamp, P.; Schüssler, U.; Gabel, D.; Schinazi, R. F.; Plešek, J. *Bioorg. Med. Chem.* **2005**, 13, 4168. (c) Olejniczak, A. B.; Plešek, J.; Lesnikowski, Z. J. *Chem.—Eur. J.* **2007**, 13, 311.

(22) (a) Sibrian-Vazquez, M.; Hao, E.; Jenssen, T. J.; Vicente, M. G. H. *Biocong. Chem.* **2006**, 17, 928. (b) Hao, E.; Sibrian-Vazquez, M.; Serem, W.; Gamo, J. C.; Fronczek, F. R.; Vicente, M. G. H. *Chem.—Eur. J.* **2007**, 13, 9035. (c) Li, F.; Fronczek, F. R.; Vicente, M. G. H. *Tetrahedron Lett.* **2008**, 49, 4828.

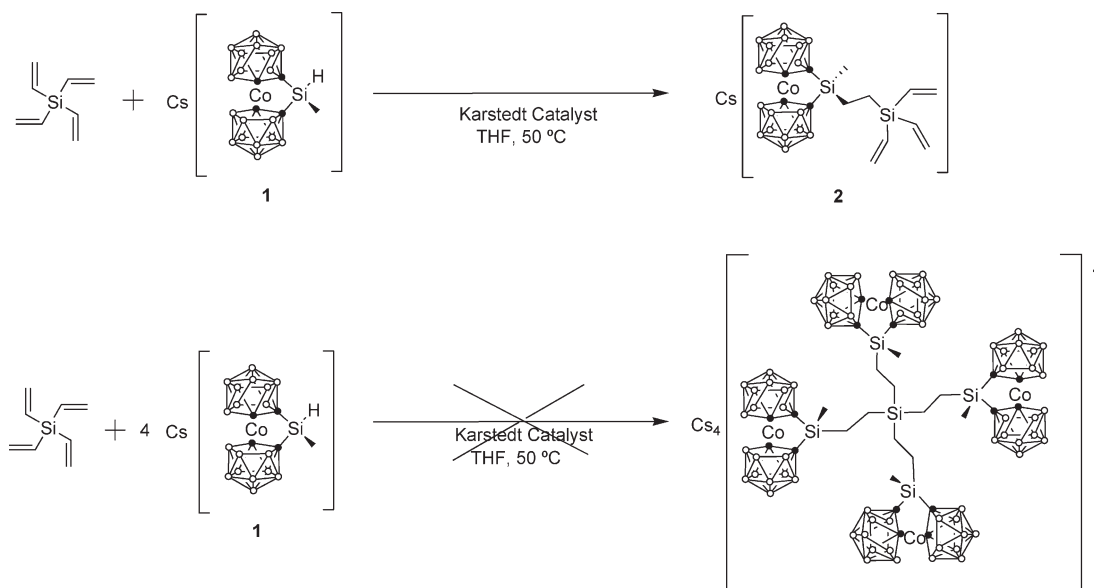
(23) Plešek, J.; Hermanek, S.; Franken, A.; Cisarova, I.; Nachtigal, Ch. *Collect. Czech. Chem. Commun.* **1997**, 62, 47.

(24) Llop, J.; Masalles, C.; Viñas, C.; Teixidor, F.; Sillanpää, R.; Kivekäs, R. *Dalton Trans.* **2003**, 556.

(25) Marciniak, B. Hydrosilylation: A Comprehensive Review on Recent Advances. In *Advances in Silicon Science*; Matisons, J., Ed.; Springer: The Netherlands, 2009; Vol. 1.

(26) (a) Juárez-Pérez, E. J.; Viñas, C.; González-Campo, A.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Núñez, R. *Chem.—Eur. J.* **2008**, 14, 4924. (b) Juárez-Pérez, E. J.; Teixidor, F.; Viñas, C.; Núñez, R. *J. Organomet. Chem.* **2009**, 694, 1764.

Scheme 1. Preparation of Compound 2 by Hydrosilylation of Tetravinylsilane with the Metallacarborane 1



the cyclosiloxane dendrimers 1G-TMViCTS(SiVi)₄ and 1G-TMViCTS(SiVi)₈, shown in Schemes 1–3, were prepared using a divergent methodology by successive alkenylation and hydrosilylation steps with Karstedt catalyst.^{3a,3c,3m}

All these starting materials have been hydrosilylated by using the C_c-substituted cobaltabisdicarbollides functionalized with the Si–H group, Cs[1,1'-μ-SiMeH-3,3'-Co(1,2-C₂B₉H₁₀)₂], **1**.²⁶ The hydrosilylation reaction of 1 equiv of **1** with 1 equiv of tetravinylsilane, in the presence of catalytic amounts of Karstedt catalyst in THF at 50 °C, afforded the trifunctional molecule **2** in 77% yield (Scheme 1). Thus, applying a 1:1 ratio of reagents, only one vinyl group from the tetravinylsilane was hydrosilylated. However, when a 4:1 ratio of **1**/tetravinylsilane was used under the same conditions, a complex mixture of di- and trihydrosilylated products was obtained according to the ¹H NMR, where residual vinyl protons were always observed. Attempts to achieve the tetrafunctionalization of tetravinylsilane by changing the temperature, the solvent (i.e., toluene), catalyst, reaction times, etc., were also carried out, but unsuccessful results were obtained. Nevertheless, the tetrafunctionalized compound was never obtained (Scheme 1). To our knowledge, the same problem was already observed by A. Otero and co-workers for the hydrosilylation of tetravinylsilane with a silyl-containing *ansa*-metallocene;²⁷ in this case even using extreme stoichiometries, only the monofunctionalization was achieved. In our opinion, probably the steric bulk of the cobaltabisdicarbollide causes the incomplete hydrosilylation and restricts the number of metallacarborane units that can be introduced in the core molecule. Conversely, when the reaction of **1** with the vinyl-terminated carbosilane dendrimer (1G-Vi₄) was carried out in a 4:1 ratio using the Karstedt catalyst in THF at 50 °C, the corresponding polyanionic molecule peripherally functionalized with cobaltabisdicarbollide anions was obtained and isolated as the cesium salt to give **3** in 51% yield (Scheme 2). Thus, the hydrosilylation of all vinyl functions was possible, thus

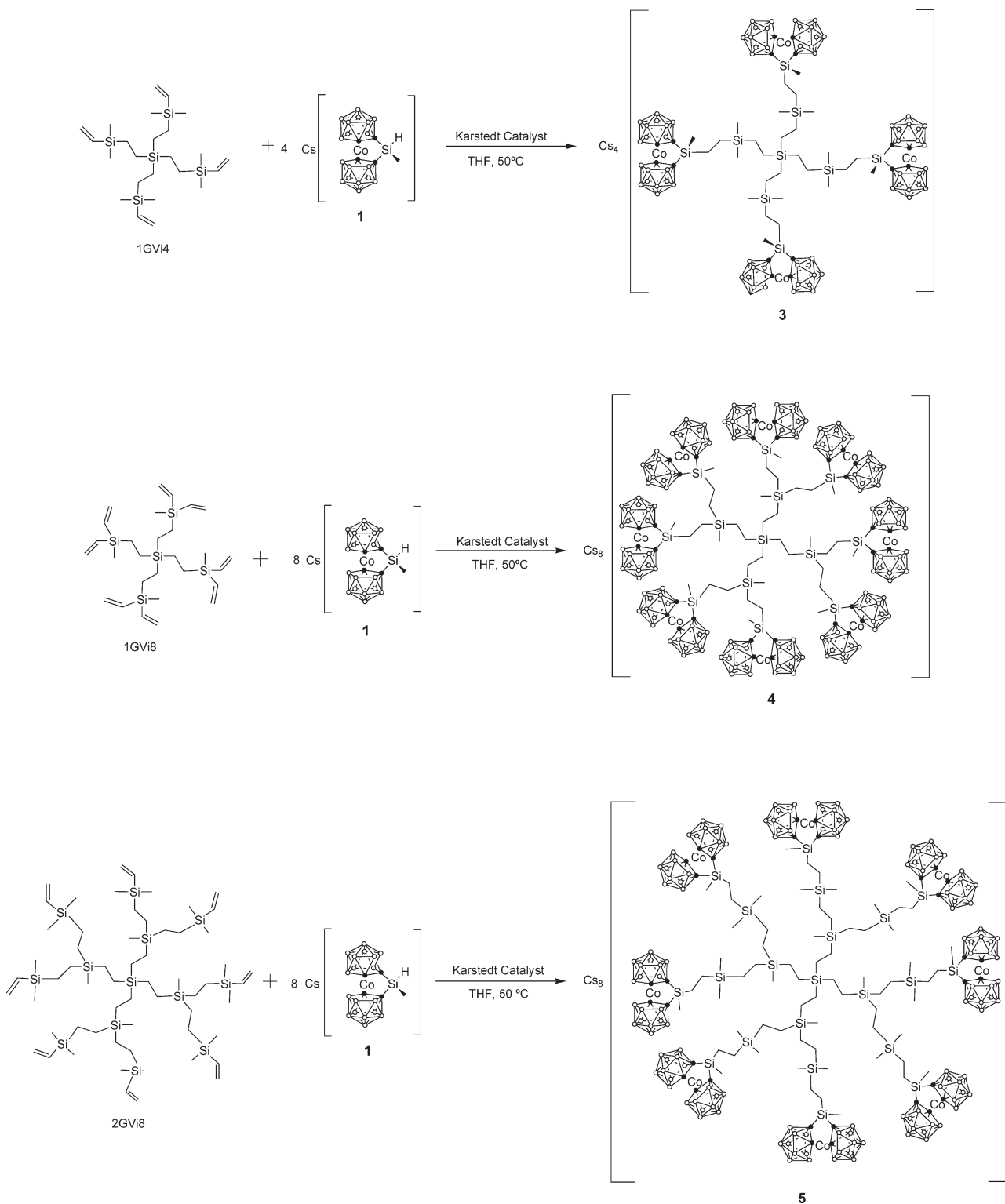
binding the four cobaltabisdicarbollide complexes to the molecule. In the same way, **1** reacted with 1G-Vi₈ and 2G-Vi₈ to give dendrimers **4** and **5**, respectively, in which eight cobaltabisdicarbollide anions are placed on the dendrimeric surface (Scheme 2). These metallodendrimers were isolated as cesium salts by precipitation with hexane in 41 and 62% yield, respectively. The reactions were carried out using longer reaction times than those used for hydrosilylation with conventional organosilanes. Carbosiloxane dendrimers **6**, **7**, and **8** were obtained in 47, 55, and 54% yield, respectively, by the reaction of **1** with TMViCTS, 1G-TMViCTS(SiVi)₄, and 1G-TMViCTS(SiVi)₈, in a 4:1 or 8:1 ratio, using similar conditions to those for the previous carbosilane dendrimers (Scheme 3). In all cases, the binding of **1** to the vinyl-terminated dendrimers was mainly monitored by ¹H NMR spectroscopy, following the disappearance of the vinyl protons. In addition, other evidence was the resonances corresponding to C_c-H and C_c-Si-CH₃ in the prepared compounds, which were shifted with respect to the starting **1**.

By using Monte Carlo simulations, the steric hindrance caused by peripheral groups located in the starting carbosilane dendrimers has been estimated (see Supporting Information).

Characterization of Carbosilane and Carbosiloxane Metallodendrimers. The novel trifunctional molecule **2** and dendrimeric structures **3**, **4**, **5**, **6**, **7**, and **8** were characterized by FT-IR, UV-vis, ¹H, ¹¹B, ¹³C, and ²⁹Si NMR spectroscopies, and mass spectrometry in some cases, which confirmed the proposed structures. The IR spectra present typical ν(B–H) strong bands for *closo* clusters around 2550 cm⁻¹ and intense bands near 1257 cm⁻¹ corresponding to δ(Si–CH₃). In addition, for **6**, **7**, and **8** intense bands near 1090 cm⁻¹ corresponding to ν(Si–O) are observed. In all compounds the characteristic band at 2110 cm⁻¹ due to ν(Si–H) is not present, indicating total hydrosilylation. The ¹H{¹¹B} NMR spectrum of **2** shows two resonances centered at δ 6.12 and 5.82 ppm attributed to the vinyl protons. In all compounds, broad resonances around 4.50 ppm corresponding to the C_c-H protons of the cobaltabisdicarbollide are observed. The ¹H{¹¹B} and ¹³C{¹H} NMR spectra exhibit resonances at low frequencies for the Si–CH₃ group (Table S2 in the

(27) (a) Antiñolo, A.; Fajardo, M.; Gómez-Ruiz, S.; López-Solera, I.; Otero, A.; Prashar, S. *Organometallics* **2004**, *23*, 4062. (b) Gómez-Ruiz, S.; Prashar, S.; Fajardo, M.; Antiñolo, A.; Otero, A.; Maestro, M.; Volkis, V.; Eisen, M.; Pastor, C. *Polyhedron* **2005**, *24*, 1298.

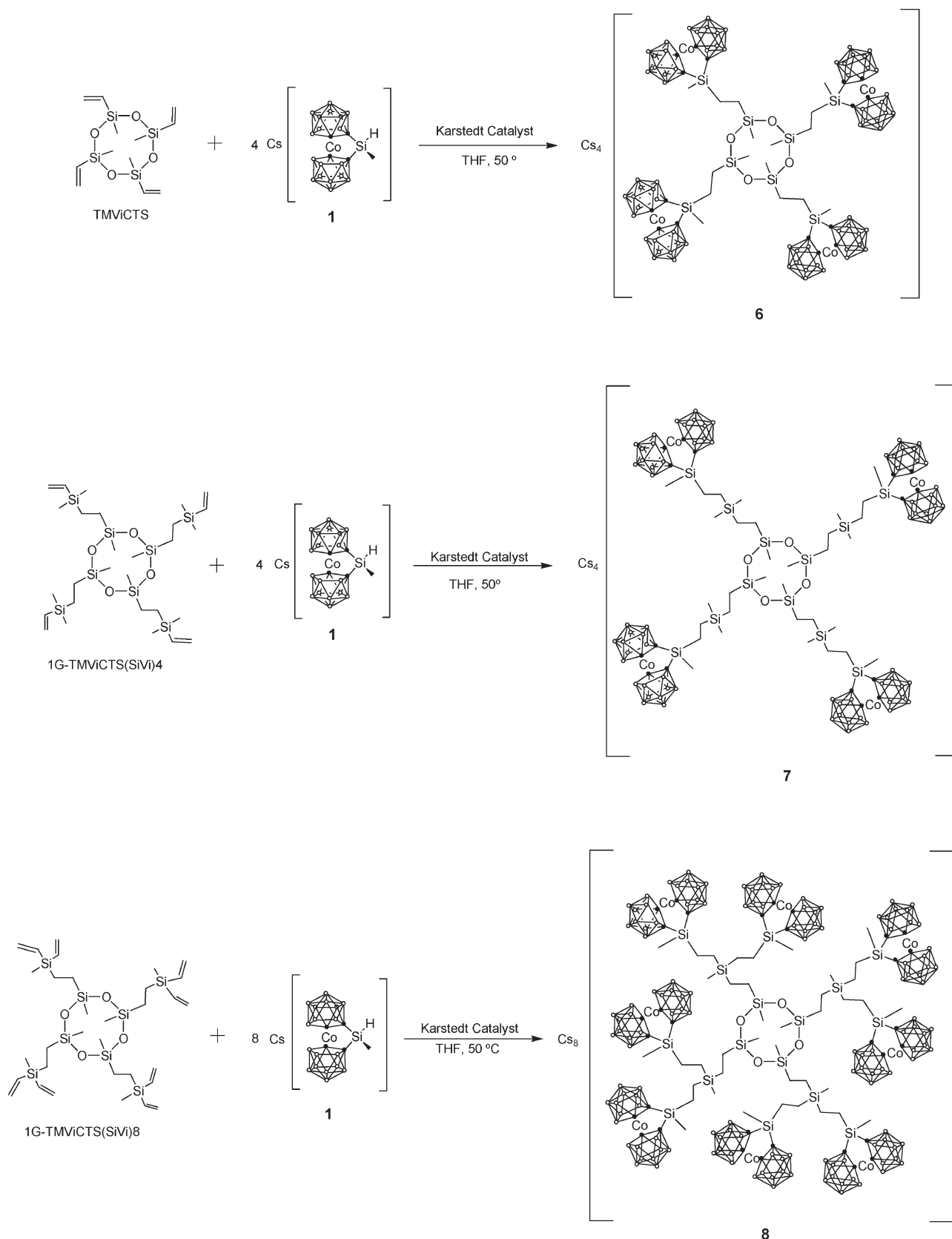
Scheme 2. Preparation of Carbosilane Dendrimers 3, 4, and 5



Supporting Information), $-\text{CH}_2-$ proton resonances appear in the range 0.49 to 0.84 ppm, and the $-\text{CH}_2-$ carbons are displayed from 2.44 to 8.98 ppm. The $-\text{CH}_2-$ protons have not been assigned due to the complexity of the signals. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for all dendrimers show resonances at 56.16 and 40.99 ppm attributed to the C_c-H and C_c-Si atoms, respectively (Table S2 in the Supporting Information). For monomer 2 the presence of vinyl functions was also confirmed by resonances at 134.51 and

134.22 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectra for compounds 2–8 are very similar, with bands in a typical range, from +8.3 to –22.0 ppm, indicative of cobaltabisdicarbollide derivatives,²⁸ with the general pattern 2:2:4:4:2:2:2 (Figure 1). Due to the similarity of these

(28) (a) Tood, L. J. *Progress in NMR Spectroscopy*; Pergamon Press Ltd., 1979; Vol. 13, p 87. (b) Rojo, I.; Teixidor, F.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Chem.—Eur. J.* **2004**, *10*, 5376.

Scheme 3. Preparation of Carbosiloxane Dendrimers 6, 7, and 8

$^{11}\text{B}\{^1\text{H}\}$ NMR spectra to that of the reported [1,1'- μ -SiMe₂-3,3'-Co(1,2-C₂B₉H₁₀)₂], **9**,²⁶ we have been able to assign each specific resonance to the corresponding boron atom. Figure 1 shows the $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of **1**, **2**, **3**, **5**, and **9**.

Noticeably, starting **1** presents a higher asymmetry that is reflected in the higher number of signals in the spectrum. Nevertheless, upon hydrosilylation, in dendrimers **3** and **5** some of the resonances are overlapped to only one, as

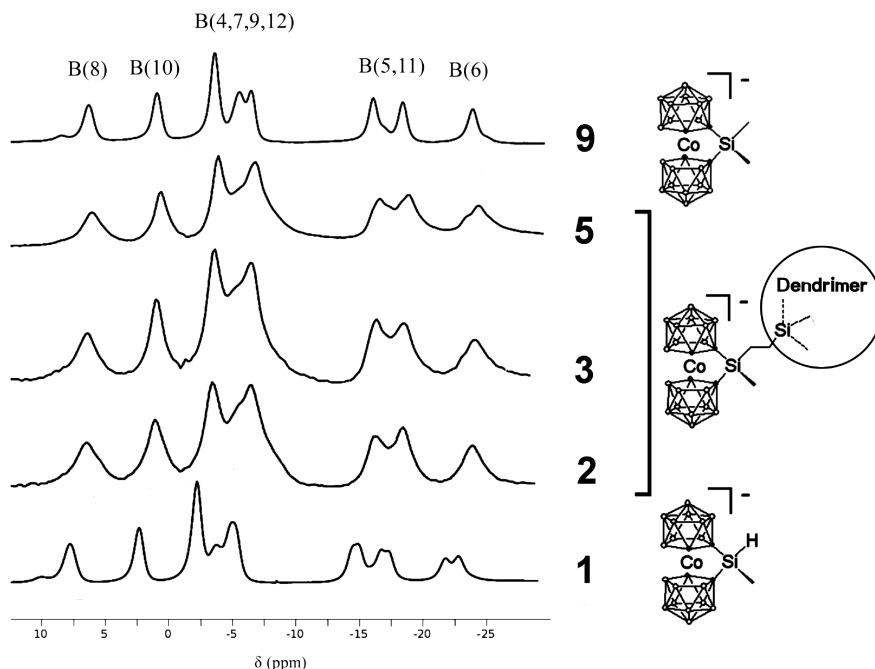


Figure 1. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra for compounds **1**, **2**, **3**, **5**, and **9**.

observed in Figure 1. In the $^{29}\text{Si}\{^1\text{H}\}$ NMR, all resonances were assigned on the basis of the chemical shifts and the peak intensities. For **2** and the first generation of the cyclosiloxane dendrimer **6**, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra exhibit two signals, whereas three resonances are observed for the rest of the dendrimers (Table S3 in the Supporting Information). The resonances due to $\text{Si}-\text{C}_{\text{cluster}}$ appear between 11.15 and 12.15 ppm, shifted around 8.5 ppm downfield with respect to the starting compound **1** ($\delta_{\text{Si}} = 2.94$ ppm). In fact, these resonances have been easily assigned by comparison with their homologue, **9** ($\delta_{\text{Si}} = 13.98$ ppm).²⁶ The Si_{core} atoms appear in the region 5.88 to 11.80 ppm for **2–5** and at higher field, around -20 ppm, for cyclosiloxanes **6–8**, in which the Si_{core} are bonded to the oxygen atom. The spectra of **3**, **4**, **5**, **7**, and **8** exhibit additional peaks, in the range 6.65–9.78 ppm, that correspond to the Si atoms of the dendrimer branches.

The UV–vis spectra of these dendrimers were measured in DMSO and acetonitrile and look very similar to that of **1**. The maximum absorbance around 310 nm can be attributed to the presence of the silyl bridge ($\mu\text{-SiR}_2$) between the dicarbollide ligands, as was already reported for **1**.²⁶ This maximum at 310 nm is different from that observed at 270 nm for the unsubstituted $\text{Cs}[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.²⁹ A second absorbance at 462 nm is due to the d–d transition in the Co metal of the cobaltabisdicarbollide **1**, showing a bathochromic shift with respect to the signal at 445 nm exhibited for $\text{Cs}[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.²⁹ Figure 2 shows the UV–vis spectra in acetonitrile for **2**, **5**, and **7**, which contain one, eight, and four cobaltabisdicarbollide moieties, respectively.

Two different mass spectrometry techniques have been used for the characterization of compounds: MALDI-TOF and electrospray (ESI). The formula of **2** was well established by using the MALDI-TOF mass spectrometry in the negative-ion mode without matrix, in which the molecular ion peak appears at $m/z = 502.2$, being in perfect accordance

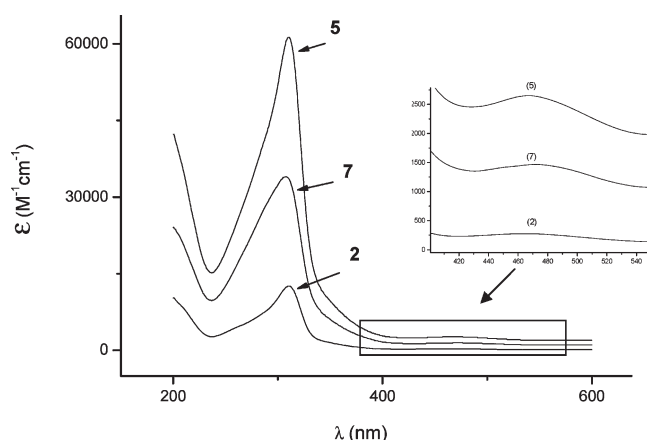


Figure 2. UV–vis spectra in acetonitrile for compounds **2**, **5**, and **7**.

with the calculated pattern (Figure S3 in the Supporting Information). The ESI mass spectrum of **3** was recorded in $\text{CHCl}_3/\text{CH}_3\text{OH}$ and shows a signal at $m/z = 2490.2$ corresponding to $[(\text{M} - \text{H}) + \text{H}_2\text{O}]^-$. Nevertheless, MALDI-TOF determinations for the higher molecular weight metallodendrimers have been of difficult interpretation, due to the fragmentation of compounds by breaking the molecule into smaller parts. The technique then supports,³⁰ although does not confirm, the formation of dendrimeric species. Therefore, we have tried to assign the peaks that in more cases are fragments in high percentage; for example the peak at 324.2 is due to $[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ and the peak at 393.4 is assigned to the fragment $[\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})\text{Si}(\text{CH}_3)(\text{CH}_2)]$. Furthermore, the presence of trapped solvent molecules has been observed.

(29) Rojo, I.; Teixidor, F.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Chem.—Eur. J.* **2003**, *9*, 4311.

(30) (a) Teixidor, F.; Pedrajas, J.; Rojo, I.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Sivaev, I.; Bregadze, V.; Sjöberg, S. *Organometallics* **2003**, *22*, 3414–3423. (b) Farràs, P.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Viñas, C.; Grüner, B.; Cisarova, I. *Inorg. Chem.* **2008**, *47*, 9497.

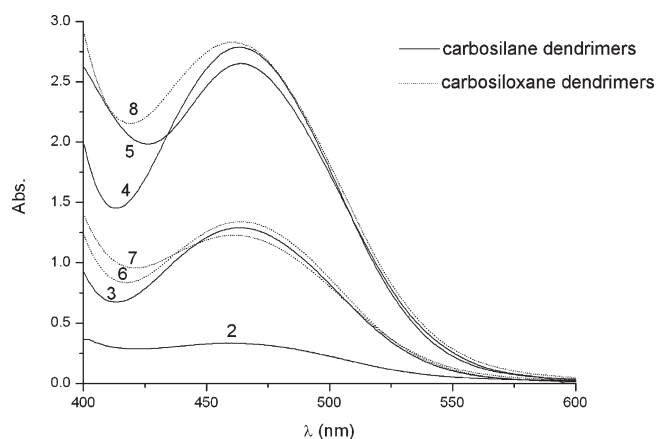
Table 1. Number of Metallacarboranes Calculated of the Cobaltabisdicarbollide-Containing Dendrimers Using the Lambert–Beer Law at 310 and 462 nm in DMSO

compound	theoretical no. of cobaltabisdicarbollides	ϵ_{310} (nm)	calcd ^a no. of cobaltabisdicarbollides	ϵ_{462} (nm)	calcd ^a no. of cobaltabisdicarbollides
2	1	$\epsilon_0 = 11\,576$		$\epsilon_0 = 333$	
3	4	51 253	4.4 ± 0.5	1278	3.8 ± 0.2
4	8	81 897	7.1 ± 0.8	2772	8.3 ± 0.3
5	8	65 219	5.6 ± 0.8	2626	7.9 ± 0.3
6	4	38 809	3.4 ± 0.4	1227	3.7 ± 0.2
7	4	39 923	3.4 ± 0.5	1340	4.0 ± 0.2
8	8	93 386	8.1 ± 0.6	2822	8.5 ± 0.4

^a ϵ/ϵ_0 represents the experimental cobaltabisdicarbollides number calculated from the Lambert–Beer law.

Elemental analyses (EA) were performed for metallodendrimers; however, in some cases it was difficult to obtain reliable results, probably due to the presence of a high boron content. Nevertheless, the problem of obtaining good results for EA in boron-containing anions has been previously reported by Gabel et al.³¹

Indirect Identification Method Based on UV–Vis Spectroscopic Measurements to Estimate the Level of Functionalization of Dendrimers with Cobaltabisdicarbollides. As mentioned before, only for compounds **2** and **3** was it possible to obtain the molecular weight using mass spectrometry. The rest of compounds showed only fragments, and in no case was the corresponding molecular ion peak observed. We have used an alternative method based on UV–vis spectroscopy, developed by Kim et al. for ethynyl silane dendrimers³² and recently used for Astruc et al.³³ to estimate the number of termini in ferrocenyl and cobalticinium dendrimers. The silyl-containing cobaltabisdicarbollides show absorption bands at 310 and 462 nm in the UV–vis spectra that follow the Lambert–Beer law (Figure S4 in the Supporting Information). The method consists of the measurement of the UV–vis absorption of solutions containing the functionalized dendrimers and studying the trend of the molar absorptivity. For our particular case the molar absorptivities (ϵ_{\max}) of the cobaltabisdicarbollide-containing dendrimers must be proportional to the number of metallacarboranes attached to the periphery. The number of cobaltabisdicarbollide fragments for each dendrimer can be estimated by comparing the absorptivity (ϵ) of the dendrimers with that obtained for monomer **2** (ϵ_0).³³ The UV–vis spectroscopic measurements were carried out in DMSO. Table 1 collects the molar absorptivity values (ϵ) obtained at 310 and 462 nm for all dendrimers and the calculated number of cobaltabisdicarbollide units using the Lambert–Beer law. The molar absorptivity increases because of the higher degree of functionalization on the dendrimeric surface. The number of cobaltabisdicarbollide units calculated using both wavelengths is close and fits quite well with the theoretical numbers, corroborating the well functionalization and the unified character of the different metallodendrimers. The graphic in Figure 3 shows the correlation between the number of metallacarboranes and the absorbance at the same concentration for the reported compounds. Thus, it can be concluded that this method is suitable to indicate the level of functionalization of the metallodendrimers. Indeed,

**Figure 3.** UV–vis spectra of compounds **2**–**8** at 1×10^{-3} M in DMSO.

the absorption at 462 nm that corresponds to the d–d transition of the C_c-silyl-substituted cobaltabisdicarbollides can also permit the experimental determination of the number of terminal metallacarborane units.

Solubility of Cesium Salts of Cobaltabisdicarbollide-Containing Metallodendrimers. With the potential applications in biomedicine previously mentioned for these anionic dendrimers in mind, it is important to know the behavior of these salts and their solubility in different solvents, especially in water. It has been reported that a challenge in the development of boron delivery agents for BNCT is to achieve boron concentrations around $20 \mu\text{g} \cdot \text{g}^{-1}$ tumor to deliver therapeutic doses of radiation to the tumor.^{19c} The cesium salts of the cobaltabisdicarbollide anion and their derivatives present good solubilities in organic polar solvents,³⁴ but a poor solubility in pure water. The solubility of Cs[Co(1,2-C₂B₉H₁₁)₂] measured by UV–vis in water at 22 °C is 9.75×10^{-4} M,³⁴ and that for the hexabromo derivative Cs[Co(1,2-C₂B₉H₈Br₃)₂] is 3×10^{-4} M,³⁵ whereas for C_c-substituted Cs[1,1'-μ-SiMeH-3,3'-Co(1,2-C₂B₉H₁₀)₂], **1**, and Cs[1,1'-μ-SiMe₂-3,3'-Co(1,2-C₂B₉H₁₀)₂], **9**, the water solubilities measured in this work are 8.5×10^{-4} and 1.9×10^{-3} M, respectively. On the other hand, salts of the cobaltabisdicarbollide with potassium, sodium, or lithium have a higher solubility in water.³⁶ In this respect, there exist two possibilities for enhancing the solubility of these anionic metallodendrimers in aqueous solutions; the first is to

(31) Justus, E.; Rischka, K.; Wishart, J.; Werner, K.; Gabel, D. *Chem.—Eur. J.* **2008**, *14*, 1918.

(32) Kim, C.; Jung, I. *J. Organomet. Chem.* **2000**, *599*, 208.

(33) (a) Ornelas, C.; Ruiz, J.; Belin, C.; Astruc, D. *J. Am. Chem. Soc.* **2009**, *131*, 590–601. (b) Ornelas, C.; Ruiz, J.; Astruc, D. *Organometallics* **2009**, *28*, 2716.

(34) Rais, J.; Selucky, P.; Kyrs, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1376.

(35) Plešek, J.; Base, K.; Mares, F.; Hanousek, F.; Stirr, B.; Hermanek, S. *Collect. Czech. Chem. Commun.* **1984**, *49*, 2776.

(36) Fanning, J. C. *Coord. Chem. Rev.* **1995**, *140*, 27.

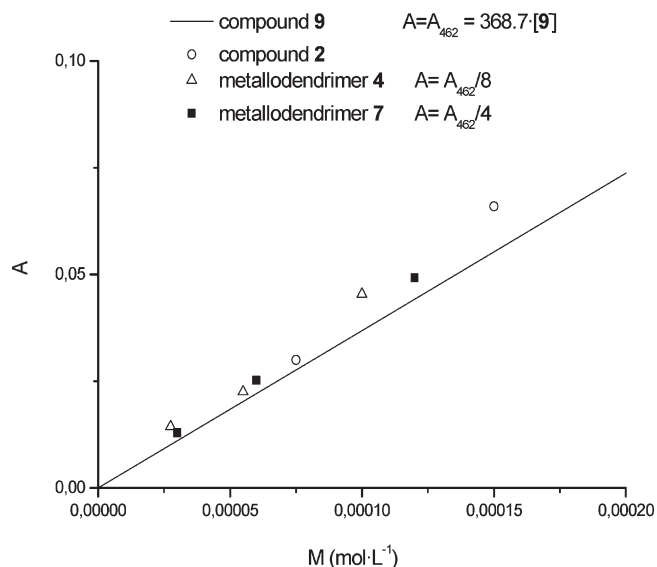


Figure 4. Calibration curve of **9** in DMSO and absorption values (*A*) toward molar concentrations (*M*) of **2**, **4**, and **7** in water/DMSO solutions.

exchange the cesium by another cation, such as sodium or potassium, using ion-exchange resins.²² However, in our case the resulting salts are difficult to isolate. The second way is to prepare a concentrated metallodendrimer solution in an organic solvent such as DMSO,^{22b} a pharmaceutical excipient commonly used,³⁷ followed by dilution with a buffer or water. This way is more convenient when the possible drug to be delivered is in cationic form because the solvent mixtures can be tailored for each anion–cation system. For testing the solubility and behavior of these cesium salts of metallodendrimers, compound **9** has been used as a reference compound to construct a calibration curve, by measuring the absorptions at 462 nm in pure DMSO for different concentrations (see Experimental Section and Figure 4). Then, different DMSO/water solutions for **4**, **7**, and **2** were prepared and their absorption values are represented in Figure 4, where it can be observed that these metallodendrimers present good solubility at different concentration ranges, depending on the degree of functionalization. Therefore, it should be possible to extrapolate this DMSO/water solubility study to other systems formed by this kind of anionic metallodendrimers combined with more complex cations with biological activity or targeting functionalities.

Conclusions

The cesium salts of the cobaltacarboranyltrivinylsilane, **2**, and two families of polyanionic cobaltabisdicarbollide-containing carbosilane and carbosiloxane metallodendrimers, **3–5** and **6–8** respectively, have been prepared by hydrosilylation of suitable dendritic molecules with Cs[1,1'-μ-SiMeH-3,3'-Co(1,2-C₂B₉H₁₀)₂], **1**, in the presence of Karstedt catalyst and optimized reaction conditions. The synthetic methodology described here has allowed us to produce in a one-pot reaction polyanionic metallodendrimers with four and eight negative charges localized on the periphery. Concerning the characterization of these compounds, it was

not possible to obtain the mass spectra for the dendrimers with the highest molecular weights; therefore UV–vis spectroscopy was used to estimate the number of peripheral cobaltabisdicarbollide units by using the Lambert–Beer law. In addition, UV–vis has also been a good tool for the study of the metallodendrimers' solubility in water/DMSO solutions, by measuring the absorptivities of different metallodendrimer concentrations.

Experimental Section

Instrumentation. IR spectra were recorded with KBr pellets or NaCl on a Shimadzu FTIR-8300 spectrophotometer. UV–vis spectroscopy was carried out with a Shimadzu UV–vis 1700 spectrophotometer, at 22 °C, using 1 cm quartz cuvettes. The electrospray-ionization mass spectra (ESI-MS) were recorded on a Bruker Esquire 3000 spectrometer using a source of ionization and an ion trap analyzer. MALDI-TOF-MS were recorded in the negative-ion mode using a Bruker Biflex MALDI-TOF [N₂ laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)] and dithranol as matrix. The ¹H, ¹H{¹¹B} NMR (300.13 MHz), ¹¹B, ¹¹B{¹H} NMR (96.29 MHz), ¹³C{¹H} NMR (75.47 MHz), and ²⁹Si{¹H} NMR (59.62 MHz) spectra were recorded on a Bruker ARX 300 spectrometer equipped with the appropriate decoupling accessories at room temperature in acetone-*d*₆ solutions. Chemical shift values for ¹¹B and ¹¹B{¹H} NMR spectra were referenced to external BF₃·OEt₂, and those for ¹H, ¹H{¹¹B}, ¹³C{¹H}, and ²⁹Si{¹H} NMR spectra were referenced to SiMe₄. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in hertz.

Materials. All manipulations were carried out under a dinitrogen atmosphere using standard Schlenck techniques. Solvents were reagent grade and were purified by distillation from appropriate drying agents before use. [Si(CH=CH₂)(CH₃)O]₄, (CH₃)₂HSiCl, (CH₃)HSiCl₂, and Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex, 2.1–2.4% platinum in vinyl-terminated polydimethylsiloxane) were purchased from ABCR and used as received. The [Si(CH=CH₂)₄] was purchased from Across. The *n*-BuLi solution (1.6 M in hexanes) was purchased from Lancaster or Aldrich and CH₂=CHMgCl (1.6 M in THF) from Aldrich. Compound Cs[1,1'-μ-SiMeH-3,3'-Co(1,2-C₂B₉H₁₀)₂], **1**, and Cs[1,1'-μ-SiMe₂-3,3'-Co(1,2-C₂B₉H₁₀)₂], **9**,²⁶ and dendrimers 1G-Vi₄, 1G-Vi₈, 2G-Vi₈, 1G-TMViCTS(SiVi)₄, and 1G-TMViCTS(SiVi)₈ were prepared according to the literature procedures.³

Synthesis of Cs[1,1'-μ-Si(CH₃)₂((CH₂)₂-Si(CH₂CH₂)₃)-3,3'-Co(1,2-C₂B₉H₁₀)₂], **2.** In a Schlenk flask, Si(CH=CH₂)₄ (72.2 mg, 0.53 mmol), 10 μL of Karstedt's catalyst, and 2 mL of THF were stirred for 10 min at room temperature. To the solution was added Cs[1,1'-μ-Si(CH₃)H-3,3'-Co(1,2-C₂B₉H₁₀)₂] (264.3 mg, 0.53 mmol), and the mixture was stirred overnight at 50 °C. Afterward, the addition of hexane to the mixture gave **2** as an orange solid. Yield: 259.1 mg, 77%. Anal. Calcd for C₁₃H₃₆B₁₈CoCsSi₂: C, 24.59; H, 5.71. Found: C, 24.24; H, 5.67. ¹H NMR: δ 6.12 (m, 3H, –CH=CH₂), 5.83–5.81 (m, 6H, –CH=CH₂), 4.49 (br s, 2H, C_c-H), 0.81–0.76 (m, 4H, –Si-CH₂-CH₂-Si), 0.32 (s, 3H, Si-CH₃). ¹H{¹¹B} NMR: δ 6.12 (m, 3H, –CH=CH₂), 5.83–5.81 (m, 6H, –CH=CH₂), 4.49 (br s, 2H, C_c-H), 3.39 (br s, 2H, B-H), 3.28 (br s, 2H, B-H), 3.08 (br s, 2H, B-H), 2.33 (br s, 2H, B-H), 2.20 (br s, 2H, B-H), 1.92 (br s, 2H, B-H), 1.66 (br s, 6H, B-H), 0.81–0.76 (m, 4H, –Si-CH₂-CH₂-Si), 0.32 (s, 3H, Si-CH₃). ¹¹B NMR: δ 8.32 (d, ¹J(B,H) = 126 Hz, 2B), 2.98 (d, ¹J(B,H) = 135 Hz, 2B), –1.60 (d, ¹J(B,H) = 141 Hz, 4B), –3.60 (d, ¹J(B,H) = 144 Hz, 2B), –4.53 (d, ¹J(B,H) = 128 Hz, 2B), –14.19 (d, ¹J(B,H) = 155 Hz, 2B), –16.32 (d, ¹J(B,H) = 185 Hz, 2B), –21.84 (d, ¹J(B,H) = 137 Hz, 2B). ¹³C{¹H} NMR: δ 134.51 (CH₂=CH–), 134.22 (CH₂=CH–),

(37) (a) Buggins, T. R.; Dickinson, P. A.; Taylor, G. *Adv. Drug Delivery Rev.* **2007**, *59*, 1482. (b) Himmel, H. M. *J. Pharmacol. Toxicol. Methods* **2007**, *56*, 145.

55.30 (C_c -H), 40.99 (C_c -Si), 4.14 ($-CH_2-$), 3.35 ($-CH_2-$), -7.72 (Si-CH₃). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ 12.15 (μ -Si- C_{cluster}), 11.80 (Si_{core}). FTIR (KBr), cm^{-1} : 3051 ($\nu(C_c-H)$), 3008 ($\nu(C_{\text{alkenyl}}-H)$), 2943 ($\nu(C_{\text{alkyl}}-H)$), 2885 ($\nu(C_{\text{alkyl}}-H)$), 2550 ($\nu(B-H)$), 1257 ($\delta(\text{Si}-CH_3)$). MALDI-TOF-MS m/z : 324.2 ($[\text{Co}(1,2-C_2B_9H_{11})]^-$, 17%), 393.2 ($[\text{Co}(1,2-C_2B_9H_{10})\text{Si}(\text{CH}_3)(CH_2)]$, 2%), 502.2 (M - Cs, 100%).

Synthesis of $[\text{Cs}_4\{2\text{G}-[1,1'-\mu\text{-Si}(\text{CH}_3)(\text{CH}_2\text{CH}_2)-3,3'-\text{Co}(\text{C}_2\text{B}_9\text{H}_{10})_2\}_4]$, **3.** In a Schlenk flask, 1G-Vi₄ (56.0 mg, 0.12 mmol), 10 μL of Karstedt's catalyst, and 2 mL of THF were stirred for 10 min at room temperature. To the solution was added Cs[1,1'- μ -Si(CH₃)H-3,3'-Co(1,2-C₂B₉H₁₀)₂] (239.4 mg, 0.48 mmol), and the mixture was stirred overnight at 50 °C. Then, the addition of a solution of hexane to the mixture gave **3** as an orange solid. Yield: 150.7 mg, 51%. Anal. Calcd for C₄₄H₁₄₈B₇₂Co₄Si₉: C, 21.34; H, 6.02. Found: C, 22.38; H, 6.16. ^1H NMR: δ 4.51 (br s, 8H, C_c -H), 0.49 (m, 32H, $-Si-CH_2-CH_2-Si$), 0.32 (s, 12H, Si-CH₃), 0.01 (s, 24H, Si-CH₃). $^1\text{H}\{^{11}\text{B}\}$ NMR: δ 4.51 (br s, 8H, C_c -H), 0.49 (m, 32H, $-Si-CH_2-CH_2-Si$), 0.32 (s, 12H, Si-CH₃), 3.39 -1.59 (br, 80 H, B-H), 0.01 (s, 24H, Si-CH₃). ^{11}B NMR: δ 8.15 (d, $^1J(\text{B,H}) = 110$ Hz, 2B), 2.93 (d, $^1J(\text{B,H}) = 132$ Hz, 2B), -1.54 (d, $^1J(\text{B,H}) = 145$ Hz, 4B), -4.54 (d, $^1J(\text{B,H}) = 113$ Hz, 4B), -14.61 (d, $^1J(\text{B,H}) = 185$ Hz, 2B), -16.54 (d, $^1J(\text{B,H}) = 178$ Hz, 2B), -21.81 (d, $^1J(\text{B,H}) = 153$ Hz, 2B). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 55.55 (C_c -H), 41.33 (C_c -Si), 6.49 ($-CH_2-$), 5.05 (Si-CH₂), 4.07 (Si-CH₂), 2.44 (Si-CH₂), -5.11 (Si-CH₃), -7.72 (Si-CH₃). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ 11.98 (μ -Si- C_{cluster}), 6.65 (Si_{branch}), 5.88 (Si_{core}). FTIR (KBr), cm^{-1} : 3062 ($\nu(C_c-H)$), 2950 ($\nu(C_{\text{alkyl}}-H)$), 2905 ($\nu(C_{\text{alkyl}}-H)$), 2550 ($\nu(B-H)$), 1257 ($\delta(\text{Si}-CH_3)$). ESI-MS m/z : 2490.2 (M + H₂O, 2%).

Synthesis of $[\text{Cs}_8\{2\text{G}-[1,1'-\mu\text{-Si}(\text{CH}_3)(\text{CH}_2\text{CH}_2)-3,3'-\text{Co}(\text{C}_2\text{B}_9\text{H}_{10})_2\}_8]$, **4.** In a Schlenk flask, 1G-Vi₈ (32.7 mg, 0.062 mmol), 10 μL of Karstedt's catalyst, and 2 mL of THF were stirred for 10 min at room temperature. To the solution was added Cs[1,1'- μ -Si(CH₃)H-3,3'-Co(1,2-C₂B₉H₁₀)₂] (246.6 mg, 0.496 mmol), and the mixture was stirred for 40 h at 50 °C. Then, 10 mL of CH₂Cl₂ was added to produce two solvent phases. The halogenated solvent was discarded by decantation. To the other, oily, dark orange phase was added 10 mL of hexane to give **4** as an orange solid. Yield: 114.5 mg, 41%. Anal. Calcd for C₆₈H₂₄₄B₁₄₄Co₈Cs₈Si₁₃: C, 18.07; H, 5.44. Found: C, 20.25; H, 5.88. ^1H NMR: δ 4.50 (br s, 16H, C_c -H), 0.52 (m, 48H, $-Si-CH_2-CH_2-Si$), 0.32 (s, 24H, Si-CH₃), 0.09 (s, 12H, Si-CH₃). $^1\text{H}\{^{11}\text{B}\}$ NMR: 4.50 (br s, 16H, C_c -H), 3.39 (br s, 16H, B-H), 3.28 (br s, 16H, B-H), 3.08 (br s, 16H, B-H), 2.33 (br s, 16H, B-H), 2.20 (br s, 16H, B-H), 1.92 (br s, 16H, B-H), 1.66 (br s, 48H, B-H), 0.52 (m, 48H, $-Si-CH_2-CH_2-Si$), 0.32 (s, 24H, Si-CH₃), 0.09 (s, 12H, Si-CH₃). ^{11}B NMR: δ 6.96 (d, $^1J(\text{B,H}) = 119$ Hz, 2B), 1.89 (d, $^1J(\text{B,H}) = 129$ Hz, 2B), -2.65 (d, $^1J(\text{B,H}) = 110$ Hz, 4B), -5.60 (d, $^1J(\text{B,H}) = 156$ Hz, 2B), -16.13 (d, $^1J(\text{B,H}) = 166$ Hz, 2B), -17.56 (d, $^1J(\text{B,H}) = 175$ Hz, 2B), -22.95 (d, $^1J(\text{B,H}) = 147$ Hz, 2B). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 55.32 ($C_{\text{cluster}}-H$), 41.24 ($C_{\text{cluster}}-Si$), 8.49, 7.18, 4.13, 3.50 ($-CH_2-$), -1.09 (Si-CH₃), -7.63 ($C_{\text{cluster}}-Si-CH_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ 11.73 (μ -Si- C_{cluster}), 9.78 (Si_{branch}), 8.28 (Si_{core}). FTIR (KBr), cm^{-1} : 3051 ($\nu(C_{\text{cluster}}-H)$), 2958 ($\nu(C_{\text{alkyl}}-H)$), 2905 ($\nu(C_{\text{alkyl}}-H)$), 2557 ($\nu(B-H)$), 1257 ($\delta(\text{Si}-CH_3)$). MALDI-TOF-MS m/z : 324.2 ($[\text{Co}(1,2-C_2B_9H_{11})]^-$, 100%), 393.2 ($[\text{Co}(1,2-C_2B_9H_{10})\text{Si}(\text{CH}_3)(CH_2)]$, 18%), 435.7 ((M + MeOH)/8, 16%).

Synthesis of $[\text{Cs}_8\{3\text{G}-[1,1'-\mu\text{-Si}(\text{CH}_3)-3,3'-\text{Co}(\text{C}_2\text{B}_9\text{H}_{10})_2\}_8]$, **5.** This compound was prepared using the same procedure as for **4**, by using 2G-Vi₈ (39.0 mg, 0.032 mmol), 10 μL of Karstedt's catalyst, and Cs[1,1'- μ -Si(CH₃)H-3,3'-Co(1,2-C₂B₉H₁₀)₂] (127.7 mg, 0.256 mmol) in 2 mL of THF. The mixture was stirred for 36 h at 50 °C. After workup, **5** was obtained as an orange solid. Yield: 103.4 mg, 62%. Anal. Calcd for C₁₀₀H₃₂₄B₁₄₄-Co₈Cs₈Si₂₁: C, 23.06; H, 6.27. Found: C, 24.67; H, 6.65. ^1H NMR: δ 4.50 (br s, 16H, C_c -H), 0.52 (m, 80H, $-Si-CH_2-CH_2-Si$), 0.31 (s, 24H, Si-CH₃), 0.10 (br s, 36H, Si-CH₃). $^1\text{H}\{^{11}\text{B}\}$

NMR: δ 4.50 (br s, 16H, C_c -H), 3.39 (br s, 16H, B-H), 3.28 (br s, 16H, B-H), 3.08 (br s, 16H, B-H), 2.33 (br s, 16H, B-H), 2.20 (br s, 16H, B-H), 1.92 (br s, 16H, B-H), 1.66 (br s, 48H, B-H), 0.52 (m, 80H, $-Si-CH_2-CH_2-Si$), 0.31 (s, 24H, Si-CH₃), 0.10 (br s, 24H, Si-CH₃). ^{11}B NMR: δ 7.58 (d, $^1J(\text{B,H}) = 131$ Hz, 2B), 2.06 (d, $^1J(\text{B,H}) = 150$ Hz, 2B), -2.42 (d, $^1J(\text{B,H}) = 150$ Hz, 4B), -5.02 (d, $^1J(\text{B,H}) = 131$ Hz, 2B), -15.00 (d, $^1J(\text{B,H}) = 169$ Hz, 2B), -17.27 (d, $^1J(\text{B,H}) = 188$ Hz, 2B), -22.80 (d, $^1J(\text{B,H}) = 169$ Hz, 2B). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 55.30 ($C_{\text{cluster}}-H$), 41.08 ($C_{\text{cluster}}-Si$), 8.52, 6.60, 4.34, 4.10, 3.55, 3.11 ($-CH_2-$), -1.13 (Si-CH₃), -5.02 (Si-CH₃), -7.77 ($C_{\text{cluster}}-Si-CH_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ 11.52 (μ -Si- C_{cluster}), 8.03, 6.32 (Si_{branch}). FTIR (KBr), cm^{-1} : 3067 ($\nu(C_{\text{cluster}}-H)$), 2955 ($\nu(C_{\text{alkyl}}-H)$), 2905 ($\nu(C_{\text{alkyl}}-H)$), 2550 ($\nu(B-H)$), 1257 ($\delta(\text{Si}-CH_3)$). MALDI-TOF-MS m/z : 324.1 ($[\text{Co}(1,2-C_2B_9H_{11})]^-$, 100%), 393.2 ($[\text{Co}(1,2-C_2B_9H_{10})\text{Si}(\text{CH}_3)(CH_2)]$, 16%), 599.7 ((M + 2dithranol + 6MeOH)/8, 53%), 633.7 ((M + 4(dithranol + H₂O)/8, 42%).

Synthesis of Cyclosiloxane Dendrimer $[\text{Cs}_4\{1\text{G}-[1,1'-\mu\text{-Si}(\text{CH}_3)-3,3'-\text{Co}(\text{C}_2\text{B}_9\text{H}_{10})_2\}_4]$, **6.** This compound was prepared using the same procedure as for **4**, by using 1,3,5,7-tetramethylvinylcyclotetrasiloxane (19.4 mg, 0.056 mmol), 10 μL of Karstedt's catalyst, and Cs[1,1'- μ -Si(CH₃)H-3,3'-Co(1,2-C₂B₉H₁₀)₂] (111.7 mg, 0.224 mmol) in 2 mL of THF. After workup, **6** was obtained as an orange solid. Yield: 61.6 mg, 47%. ^1H NMR: δ 4.51 (br s, 8H, C_c -H), 0.57 (m, 16H, $-Si-CH_2-CH_2-Si$), 0.34 (s, 12H, Si-CH₃), 0.16 (s, 12H, Si-CH₃). $^1\text{H}\{^{11}\text{B}\}$ NMR: 4.51 (br s, 16H, C_c -H), 3.39 (br s, 16H, B-H), 3.28 (br s, 16H, B-H), 3.08 (br s, 16H, B-H), 2.33 (br s, 16H, B-H), 2.20 (br s, 16H, B-H), 1.92 (br s, 16H, B-H), 1.66 (br s, 48H, B-H), 0.57 (m, 16H, $-Si-CH_2-CH_2-Si$), 0.34 (s, 12H, Si-CH₃), 0.16 (s, 12H, Si-CH₃). ^{11}B NMR: δ 7.55 (d, $^1J(\text{B,H}) = 136$ Hz, 2B), 2.02 (d, $^1J(\text{B,H}) = 169$ Hz, 2B), -2.75 (d, $^1J(\text{B,H}) = 141$ Hz, 4B), -5.43 (d, $^1J(\text{B,H}) = 144$ Hz, 2B), -15.79 (d, $^1J(\text{B,H}) = 155$ Hz, 2B), -17.08 (d, $^1J(\text{B,H}) = 150$ Hz, 2B), -23.10 (d, $^1J(\text{B,H}) = 131$ Hz, 2B). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 56.16 ($C_{\text{cluster}}-H$), 41.93 ($C_{\text{cluster}}-Si$), 8.44 ($-CH_2-$), 4.21 ($-CH_2-$), -1.04 , (O-Si-CH₃), -6.70 ($C_{\text{cluster}}-Si-CH_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ 11.85 (μ -Si- C_{cluster}), -20.53 (O-Si). FTIR (KBr), cm^{-1} : 3059 ($\nu(C_{\text{cluster}}-H)$), 2955 ($\nu(C_{\text{alkyl}}-H)$), 2905 ($\nu(C_{\text{alkyl}}-H)$), 2550 ($\nu(B-H)$), 1257 ($\delta(\text{Si}-CH_3)$), 1095 ($\delta(\text{Si}-O)$). MALDI-TOF-MS m/z : 324.2 ($[\text{Co}(1,2-C_2B_9H_{11})]^-$, 51%), 393.2 ($[\text{Co}(1,2-C_2B_9H_{10})\text{Si}(\text{CH}_3)(CH_2)]$, 100%), 494.4 ((M + Cs + 2H₂O)/4, 21%).

Synthesis of Cyclosiloxane Dendrimer $[\text{Cs}_4\{2\text{G}-[1,1'-\mu\text{-Si}(\text{CH}_3)-3,3'-\text{Co}(\text{C}_2\text{B}_9\text{H}_{10})_2\}_4]$, **7.** This compound was prepared using the same procedure as for **4**, by using 1G-tetra-vinylcyclotetrasiloxane (60.5 mg, 0.096 mmol), 10 μL of Karstedt's catalyst, and Cs[1,1'- μ -Si(CH₃)H-3,3'-Co(1,2-C₂B₉H₁₀)₂] (191.6 mg, 0.384 mmol) in 2 mL of THF. The mixture was stirred overnight at 50 °C. After addition and vigorous stirring of 20 mL of CH₂Cl₂, **7** was precipitated, filtered, and dried in vacuo. Yield: 138.3 mg, 55%. Anal. Calcd for C₄₈H₁₆₀B₇₂Co₄Cs₄O₄Si₁₂: C, 21.47; H, 6.01. Found: C, 20.55; H, 6.01. ^1H NMR: δ 4.50 (br s, 8H, C_c -H), 0.50 (m, 32H, $-Si-CH_2-CH_2-Si$), 0.30 (s, 12H, Si-CH₃), 0.08 (s, 12H, Si-CH₃), 0.00 (s, 24H, $-Si-CH_3$). $^1\text{H}\{^{11}\text{B}\}$ NMR: δ 4.50 (br s, 16H, C_c -H), 3.40 (br s, 16H, B-H), 3.26 (br s, 16H, B-H), 3.05 (br s, 16H, B-H), 2.33 (br s, 16H, B-H), 2.21 (br s, 16H, B-H), 1.92 (br s, 16H, B-H), 1.66 (br s, 48H, B-H), 0.50 (m, 32H, $-Si-CH_2-CH_2-Si$), 0.30 (s, 12H, Si-CH₃), 0.08 (s, 12H, Si-CH₃), 0.00 (s, 24H, Si-CH₃). ^{11}B NMR: δ 7.24 (d, $^1J(\text{B,H}) = 126$ Hz, 2B), 1.81 (d, $^1J(\text{B,H}) = 135$ Hz, 2B), -2.92 (d, $^1J(\text{B,H}) = 141$ Hz, 4B), -5.70 (d, $^1J(\text{B,H}) = 144$ Hz, 2B), -15.73 (d, $^1J(\text{B,H}) = 155$ Hz, 2B), -17.50 (d, $^1J(\text{B,H}) = 185$ Hz, 2B), -23.20 (d, $^1J(\text{B,H}) = 137$ Hz, 2B). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 55.29 ($C_{\text{cluster}}-H$), 41.16 ($C_{\text{cluster}}-Si$), 8.98, 5.65, 5.05, 4.04 ($-CH_2-$), -1.05 , (O-Si-CH₃), -5.15 (Si-CH₃), -7.75 ($C_{\text{cluster}}-Si-CH_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ 11.85 (μ -Si- C_{cluster}), -20.53 (O-Si). FTIR (KBr), cm^{-1} : 3063 ($\nu(C_{\text{cluster}}-H)$), 2955 ($\nu(C_{\text{alkyl}}-H)$), 2908 ($\nu(C_{\text{alkyl}}-H)$), 2554 ($\nu(B-H)$), 1257 ($\delta(\text{Si}-CH_3)$), 1080 ($\delta(\text{Si}-O)$). MALDI-TOF-MS m/z : 324.2 ($[\text{Co}(1,2-C_2B_9H_{11})]^-$, 100%), 393.2 ($[\text{Co}(1,2-C_2B_9H_{10})\text{Si}(\text{CH}_3)(CH_2)]$, 48%).

Synthesis of Cyclosiloxane Dendrimer $\text{Cs}_8\{2\text{G}[\text{1,1}'\text{-}\mu\text{-Si}(\text{CH}_3)\text{-3,3}'\text{-Co}(\text{C}_2\text{B}_9\text{H}_{10})_2\}_8\}$, **8.** This compound was prepared using the same procedure as for **7**, by using 1G-octavinylcyclotetrasiloxane (18.0 mg, 0.024 mmol), 10 μL of Karstedt's catalyst, and $\text{Cs}\{1,1'\text{-}\mu\text{-Si}(\text{CH}_3)\text{H-3,3}'\text{-Co}(\text{1,2-C}_2\text{B}_9\text{H}_{10})_2\}$ (97.5 mg, 0.195 mmol) in 3 mL of THF. The mixture was stirred for 48 h at 50 °C. After workup, **8** was obtained as an orange solid. Yield: 62 mg, 54%. ^1H NMR: δ 4.51 (br s, 16H, $\text{C}_\text{c-H}$), 0.55 (m, 48H, $-\text{Si-CH}_2\text{-CH}_2\text{-Si-}$), 0.32 (s, 24H, Si-CH_3), 0.12 (s, 24H, Si-CH_3). $^1\text{H}\{^{11}\text{B}\}$ NMR: δ 4.51 (br s, 16H, $\text{C}_\text{c-H}$), 3.38 (br s, 16H, B-H), 3.25 (br s, 16H, B-H), 3.07 (br s, 16H, B-H), 2.30 (br s, 16H, B-H), 2.21 (br s, 16H, B-H), 1.95 (br s, 16H, B-H), 1.67 (br s, 48H, B-H), 0.55 (m, 48H, $-\text{Si-CH}_2\text{-CH}_2\text{-Si-}$), 0.32 (s, 24H, Si-CH_3), 0.12 (s, 24H, Si-CH_3). ^{11}B NMR: δ 7.60 (d, $^1J(\text{B,H}) = 132$ Hz, 2B), 2.24 (d, $^1J(\text{B,H}) = 115$ Hz, 2B), -2.54 (d, $^1J(\text{B,H}) = 131$ Hz, 4B), -5.52 (d, $^1J(\text{B,H}) = 130$ Hz, 2B), -15.12 (d, $^1J(\text{B,H}) = 132$ Hz, 2B), -17.46 (d, $^1J(\text{B,H}) = 151$ Hz, 2B), -22.98 (d, $^1J(\text{B,H}) = 124$ Hz, 2B). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 50.95 ($\text{C}_{\text{cluster-H}}$), 43.83 ($\text{C}_{\text{cluster-Si}}$), 8.57, 7.68, 5.62, 4.40 ($-\text{CH}_2-$), -0.65 , -1.82 (Si-CH_3), -7.73 ($\text{C}_{\text{cluster-Si-CH}_3}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ 11.74 ($\mu\text{-Si-C}_{\text{cluster}}$), 8.88 ($\text{Si}_{\text{branch}}$), -19.94 (O-Si). FTIR (KBr), cm^{-1} : 3061 ($\nu(\text{C}_{\text{cluster-H}}$)), 2958 ($\nu(\text{C}_{\text{alkyl-H}}$)), 2916 ($\nu(\text{C}_{\text{alkyl-H}}$)), 2552 ($\nu(\text{B-H})$), 1259 ($\delta(\text{Si-CH}_3)$), 1084 ($\delta(\text{Si-O})$). MALDI-TOF-MS m/z : 324.2 ($[\text{Co}(\text{1,2-C}_2\text{B}_9\text{H}_{10})]^-$, 2%), 393.2 ($[\text{Co}(\text{1,2-C}_2\text{B}_9\text{H}_{10})\text{Si}(\text{CH}_3)(\text{CH}_2)]^-$, 14%), 454.7 ($(\text{M} - \text{CH}_3\text{O})/8$, 49%).

UV-Vis Spectroscopy. UV-vis spectra have been measured using the following procedure: stock solutions of compounds were obtained by preparing solutions in DMSO and acetonitrile. The UV-vis absorption at 310 and 462 nm was measured in DMSO, and the molar absorptivity (ϵ) was obtained according to the relationship $\epsilon = A/M$, where M is the molar concentration of the solution (Table 1). For that, different molar concentrations of **2**, **3**, **4**, **5**, **6**, **7**, and **8** in DMSO were used to estimate the number of peripheral cobaltabisdicarbollides; the ranges are from 1×10^{-3} to 6.5×10^{-6} depending on the compound and the wavelength. For each sample, the absorbance was measured five times for the 462 nm band and three times for 310 nm. Sometimes it was necessary to make a deconvolution of the band at 310 nm to obtain an accurate absorbance value.²⁹

Test of Solubility in Water/DMSO for Cesium Salts of Metallodendrimers. Calibration Curve of **9** in DMSO (Figure 4). The UV-vis absorptions for DMSO solutions of **9** at 10^{-2} , 5×10^{-3} , 2.5×10^{-3} , 1.25×10^{-3} , 6.25×10^{-4} , 3.13×10^{-4} , 1.56×10^{-4} , 7.8×10^{-5} , 3.9×10^{-5} , and 1.95×10^{-5} M were measured

at 462 nm in order to construct the calibration curve. The Lambert-Beer law is applied and the relationship between the absorptions and concentrations has been calculated as $A_{462} = 368.8[9]$ ($R^2 = 0.9997$), where A_{462} is the absorption of the solution at 462 nm, 368.8 is the molar absorptivity ϵ ($\text{mol} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$) at 462 nm, and $[9]$ is the molar concentration ($\text{mol} \cdot \text{L}^{-1}$) for **9** in DMSO.

Solubility Tests (Table S4 in Supporting Information). Entry 1 in Table S4: 11.3 mg of **2** was dissolved in 13 mL of DMSO to give a solution of 1.37×10^{-3} M. This solution was further diluted to 4.6×10^{-4} M by addition of 25 mL of H_2O . To 1 mL of this solution was added 2 mL of pure water to give a final concentration of 1.5×10^{-4} M, with 87.9% water (w/w).

Entry 2 in Table S4: A solution of 7.5×10^{-5} M, with 93.9% water (w/w), was prepared by addition of 2 mL of water to 2 mL of the previous solution (1.5×10^{-4} M) of **2**.

Entry 3 in Table S4: 12.5 mg of **4** was dissolved in 0.25 mL of DMSO to give a concentration of 1.1×10^{-2} M. This solution was further diluted to 1.1×10^{-4} M (98.9% water) by addition of 25 mL of H_2O .

Entry 4 in Table S4: A solution of concentration 5.5×10^{-5} M, with 99.5% water (w/w), was prepared by addition of 2 mL of H_2O to 2 mL of the previous solution (1.1×10^{-4} M) of **4**.

Entry 5 in Table S4: A solution of concentration 2.8×10^{-5} M, with 99.7% water (w/w), was prepared by addition of 2 mL of H_2O to 2 mL of the previous solution (5.5×10^{-5} M) of **4**.

Entry 6 in Table S4: 24 mg of **7** was dissolved in 2 mL of DMSO to give a concentration of 4.5×10^{-3} M. This solution was further diluted to 1.2×10^{-4} M (97.4% water) by addition of 75 mL of H_2O .

Entry 7 in Table S4: A solution 6.0×10^{-5} M, with 98.7% water (w/w), was prepared by addition of H_2O (2 mL) to 2 mL of the previous solution (1.2×10^{-4} M) of **7**.

Entry 8 in Table S4: A solution 3.0×10^{-5} M, with 99.4% water, was prepared by addition of H_2O (2 mL) to 2 mL of the solution (6.0×10^{-5} M) of **7**.

Acknowledgment. This work has been supported by the CICYT (MAT2006-05339) and the Generalitat de Catalunya, 2005/SGR/00709. E.J.J.P. thanks the Ministerio de Educación y Ciencia for a FPU grant.

Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.