See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/231730662

## Facile Synthetic Routes to Phenylene and Triazine Core Based Dendritic Cobaltabisdicarbollides§

ARTICLE in ORGANOMETALLICS · JULY 2010

Impact Factor: 4.13 · DOI: 10.1021/om100365t

**CITATIONS** 

18

READS

42

## 4 AUTHORS, INCLUDING:



John Maguire
Southern Methodist University
163 PUBLICATIONS 2,529 CITATIONS

SEE PROFILE



Narayan Hosmane
Northern Illinois University
339 PUBLICATIONS 4,689 CITATIONS

SEE PROFILE

DOI: 10.1021/om100365t



# Facile Synthetic Routes to Phenylene and Triazine Core Based Dendritic Cobaltabisdicarbollides<sup>§</sup>

Barada Prasanna Dash,  $^{\dagger}$  Rashmirekha Satapathy,  $^{\dagger}$  John A. Maguire,  $^{\ddagger}$  and Narayan S. Hosmane\*,  $^{\dagger}$ 

†Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115-2862, and ‡Department of Chemistry, Southern Methodist University, Dallas, Texas 75275-0314

Received April 28, 2010

The synthesis and thermal properties of phenylene and triazine core based symmetrical macromolecules containing three to six cobaltabis(dicarbollide) clusters are reported. The zwitterionic oxonium derivative of cobaltabis(dicarbollide),  $[3,3'\text{-Co}(8\text{-C}_4H_8O_2\text{-}1,2\text{-C}_2B_9H_{10})(1',2'\text{-C}_2B_9H_{11})]$ , has been used for the synthetic transformations, and silicon tetrachloride and triflic acid were used as the cyclotrimerization reagents. Compounds containing multiple cobaltabis(dicarbollide) clusters are found to be extremely thermally stable, and only a 10-30% mass loss occurred up to 700 °C.

#### Introduction

Ever since the synthesis of the cobaltabis(dicarbollide) anion 1, [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup>, was reported by Hawthorne's research group, <sup>1</sup> its high thermal and chemical stability has made it one of the most widely used metallacarboranes<sup>2</sup> in synthetic chemistry (Figure 1).<sup>3</sup> A number of unique applications of the cobaltabis(dicarbollide) anion have also been reported. The cobaltabis(dicarbollide)—porphyrin conjugates have been evaluated as boron drug delivery platforms, <sup>4</sup> while derivatives of 1 have also been synthesized for the selective

§ Part of the Dietmar Seyferth Festschrift. Dedicated to Prof. Dietmar Seyferth for his lifetime contribution to organometallic chemistry.

removal of radionuclides.<sup>5</sup> Some other recent applications of 1 include its use in the synthesis of thermally stable conducting polymers,<sup>6</sup> coordination polymers and metal organic frameworks,<sup>7</sup> and ion selective electrodes and sensors.<sup>8</sup>

The synthesis of the zwitterionic oxonium derivative 2,  $[3,3'-Co(8-C_4H_8O_2-1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]$ , ushered in a new area of research on the synthetic chemistry of monosubstituted cobaltacarborane complexes (Figure 1). Compound 2 was first prepared by the reaction of the parent metallacarborane with Me<sub>2</sub>SO<sub>4</sub> in 1,4-dioxane,<sup>9</sup> and later the same product was obtained using BF<sub>3</sub>·OEt<sub>2</sub>. 10 Compound 2 has been shown to undergo dioxane ring-opening reactions in the presence of a variety of nucleophilic reagents, such as fluoride, chloride, and hydroxide anions, imide, cyanide, and amines. 11 Recently there have been reports on the synthesis of dendritic macromolecules that contain multiple cobaltabis(dicarbollide) clusters. These dendritic molecules were synthesized by employing hydrosilylation reactions with the C<sub>c</sub>-silyl-substituted cobaltabis(dicarbollide) derivative Cs[1,1'- $\mu$ -SiMeH-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]. <sup>12</sup> For the above-mentioned metallacarborane dendrimers UV-vis absorption was found to be a good tool for estimating the number of cobaltabis-(dicarbollide) moieties present in the molecule. <sup>12</sup> A few examples of symmetrical and dendritic compounds involving small

Seyferth for his lifetime contribution to organometallic chemistry.

\*To whom correspondence should be addressed. E-mail: hosmane@niu.edu.

<sup>(1) (</sup>a) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. J. Am. Chem. Soc. 1965, 87, 1818–1819. (b) Hawthorne, M. F.; Young, D. C.; Garrett, D. A.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. J. Am. Chem. Soc. 1968, 90, 862–868. (c) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F.; Wegner, P. A. J. Am. Chem. Soc. 1968, 90, 879–896.

<sup>(2) (</sup>a) Satapathy, R.; Dash, B. P.; Maguire, J. A.; Hosmane, N. S. *Dalton Trans.* **2010**, 39, DOI: 10.1039/c001994a. (b) Hosmane, N. S.; Maguire, J. A. *Organometallics* **2005**, 24, 1356–1389. (c) Saxena, A. K.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **1997**, 97, 2421–2462. (d) Xie, Z. *Coord. Chem. Rev.* **2002**, 231, 23–46. (e) Xie, Z. *Acc. Chem. Res.* **2003**, 36, 1–9. (f) Xie, Z. *Pure Appl. Chem.* **2003**, 75, 1335–1341.

<sup>(3)</sup> Sivaev, I. B.; Bregadze, V. I. Collect. Czech. Chem. Commun. 1999, 64, 783–805.

<sup>(4) (</sup>a) Sibrian-Vazquez, M.; Hao, E.; Timothy J. Jensen, T. J.; Vicente, M. G. H. *Bioconjugate Chem.* **2006**, *17*, 928–934. (b) Hao, E.; Vicente, M. G. H. *Chem. Commun.* **2005**, 1306–1308. (c) Hao, E.; Sibrian-Vazquez, M.; Serem, W.; Garno, J. C.; Fronczek, F. R.; Vicente, M. G. H. *Chem.—Eur. J.* **2007**, *13*, 9035–9042.

<sup>(5) (</sup>a) Plesek, J. Chem. Rev. 1992, 92, 269–278. (b) Grimes, R. N. J. Chem. Educ. 2004, 81, 657–672. (c) Vinas, C.; Gómez, S.; Bertran, J.; Teixidor, F.; Dozol, J.-F.; Rouquette, H. Inorg. Chem. 1998, 37, 3640–3643. (d) Vinas, C.; Bertran, J.; Gomez, S.; Teixidor, F.; Dozol, J.-F.; Rouquette, H.; Kivekas, R.; Sillanpaa, R. J. Chem. Soc., Dalton Trans. 1998, 2849–2854. (e) Vinas, C.; Gomez, S.; Bertran, J.; Teixidor, F.; Dozol, J.-F.; Rouquette, H. Chem. Commun. 1998, 191–192.

<sup>(6) (</sup>a) Masalles, C.; Borros, S.; Vinas, C.; Teixidor, F. *Adv. Mater.* **2002**, *14*, 449–452. (b) Masalles, C.; Llop, J.; Vinas, C.; Teixidor, F. *Adv. Mater.* **2002**, *14*, 826–829.

<sup>(7)</sup> Hardie, M. J. J. Chem. Crystallogr. 2007, 37, 69-80.

<sup>(8) (</sup>a) Stoica, A.-I.; Vinas, C.; Teixidor, F. *Chem. Commun.* **2008**, 6492–6494. (b) Stoica, A.-I.; Vinas, C.; Teixidor, F. *Chem. Commun.* **2009**, 4988–4990.

<sup>(9)</sup> Plesek, J.; Hermanek, S.; Franken, A.; Cisarova, I.; Nachtigal, C. Collect. Czech. Chem. Commun. 1997, 62, 47–56.

<sup>(10)</sup> Semioshkin, A. A.; Sivaev, I. B.; Bregadze, V. I. *Dalton Trans.* **2008**, 977–992.

<sup>(11) (</sup>a) Llop, J.; Masalles, C.; Vinas, C.; Teixidor, F.; Sillanpaa, R.; Kivekas, R. *Dalton Trans.* **2003**, 556–561. (b) Teixidor, F.; Pedrajas, J.; Rojo, I.; Vinas, C.; Kiveks, R.; Sillanp, R.; Sivaev, I.; Bregadze, V.; Sjberg, S. *Organometallics* **2003**, 22, 3414–3423.

<sup>(12) (</sup>a) Juarez-Perez, E. J.; Vinas, C.; Teixidor, F.; Nunez, R. *Organometallics* **2009**, *28*, 5550–5559. (b) Juarez-Perez, E. J.; Vinas, C.; Teixidor, F.; Santillan, R.; Farfan, N.; Abreu, A.; Yepez, R.; Nunez, R. *Macromolecules* **2010**, *43*, 150–159.

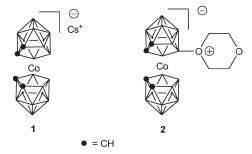


Figure 1. Cobaltabis(dicarbollide) anion 1 and its zwitterionic cyclic oxonium derivative 2.

cage carboranes (C<sub>2</sub>B<sub>4</sub> clusters) have been reported. For example, a triangular metallacarborane containing three benzene-anchored, seven-vertex ferracarborane clusters linked to a central phenyl ring via -C≡C- units was synthesized. Attachment of the  $-C \equiv C$  units to the apical boron atom of the C<sub>2</sub>B<sub>4</sub> clusters was achieved by using a Negishi-type coupling reaction. Finally a Sonogashira-type reaction of triiodobenzene with the apically substituted terminal alkynes led to the formation of the triangular metallacarborane. 13 Another attempt to use the decapitated open-faced cobaltacarborane nido- $[\eta^5-C_5H_4C(O)Cl]Co(2,3-Et_2C_2B_3H_5)$  for the synthesis of a 32-cobalt metallacarborane dendrimer was also reported by Grime's group. This was accomplished by treating the fourth-generation dendrimer diaminobutane-dend $(NH_2)_{32}$ (DAB-32) with the decapitated cobaltacarborane in the presence of trimethylamine.<sup>14</sup>

Metallodendrimers<sup>15</sup> are a class of globular macromolecules that find applications in molecular electronics, <sup>16</sup> energy conversion, <sup>16d</sup> sensing, <sup>17</sup> and catalysis<sup>18</sup> and also show electron transfer properties. <sup>16,17</sup> All these interesting applications of metallodendrimers led us to synthesize new classes of phenylene and triazine core based dendritic metallacarborane molecules containing three to six cobaltabis(dicarbollides) by employing silicon tetrachloride- and triflic acid-promoted cyclizations.

Silicon tetrachloride-mediated trimerization of aromatic ketones is a proven method for synthesis of  $C_3$ -symmetric building blocks, <sup>19</sup> and the use of this reagent for the synthesis of carborane-appended  $C_3$ -symmetrical extended  $\pi$  systems has recently been reported. <sup>19a,b</sup> The dendritic and macromolecular compounds containing multiple carborane clusters were found to be extremely thermally stable. <sup>19b,20</sup> This prompted us to study the thermal properties of the newly synthesized compounds containing multiple cobaltabis(dicarbollides).

#### **Results and Discussion**

Synthesis. The cesium salt of cobaltabis(dicarbollide) anion 1, Cs[Co(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup>, was prepared from o-carborane as per the literature procedure. The functionalization of 1 with the dioxane moiety at the 8 position led to the formation of 2,  $[3,3'-Co(8-C_4H_8O_2-1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]$ , which was carried out by refluxing 1 with excess dioxane in the presence of  $BF_3 \cdot OEt_2$ . October 2 was then used for the synthesis of symmetrical cobaltabis(dicarbollide) compounds via the nucleophilic ring-opening reactions. Symmetrical dendritic molecules are commonly synthesized by employing two methods, the convergent and divergent approaches. The convergent approach is the one in which the growth of the dendrimer starts from the exterior of the molecule and progresses inward, and finally the branching units are attached to the core. On the other hand, in the divergent method the dendrimers are synthesized from the core of the dendrimer and then continue to grow outward by repetition of coupling and activation steps.<sup>21</sup> In this paper the nucleophilic ring-opening reaction of the oxonium ring of 2 has been successfully used for both divergent and convergent approaches of synthesizing symmetrical cobaltabis-(dicarbollide) macromolecules.

The synthesis of phenylene core based symmetrical compound 6 containing three cobaltabis(dicarbollide) clusters is shown in Scheme 1. This was accomplished in two ways. In the first approach silicon tetrachloride-mediated trimerization of 4-hydoxyacetophenone led to the formation of the 1,3,5-tris(4hydroxyphenyl)benzene 4, followed by the addition of 2 in the presence of potassium carbonate, leading to the formation of 6 in 83% yield. Direct trimerization of 4-hydoxyacetophenone in the presence of silicon tetrachloride worked well for the synthesis of 4, and therefore the trimerization of 4-allyloxyacetophenone and subsequent removal of allyl groups via a palladiumcatalyzed reaction, as described in the recent literature, was not necessary. 12b Synthesis of 4 has also been previously described via a multistep synthetic procedure. <sup>22</sup> In the second approach, **2** was treated with 4-hydoxyacetophenone, which led to the formation of the ketone 5 via the ring-opening reaction, and then it was trimerized in the presence of silicon tetrachloride and ethanol to produce 6. However, the yield during the trimerization reaction was reduced to 76%.

Triflic acid-mediated cyclotrimerization of aromatic nitriles usually leads to 1,3,5-triazine core based structures.<sup>23</sup> Such triazine core based compounds find applications in the

<sup>(13)</sup> Yao, H.; Sabat, M.; Grimes, R. N. Organometallics 2002, 21, 2833–2835.

<sup>(14)</sup> Yao, H.; Grimes, R. N.; Corsini, M.; Zanello, P. *Organometallics* **2003**, *22*, 4381–4383.

<sup>(15) (</sup>a) Astruc, D.; Ornelas, C.; Ruiz, J. *Acc. Chem. Res.* **2008**, *41*, 841–856. (b) Hwag, S. H.; Shreiner, C. D.; Moorefield, C. N.; Newkome, G. R. *New J. Chem.* **2007**, *31*, 1192–1217. (c) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746. (d) Ornelas, C.; Ruiz, J.; Astruc, D. *Organometallics* **2009**, *28*, 2716–2723.

<sup>(16) (</sup>a) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219*, 545–572. (b) Gorman, C. B.; Smith, J. C. *Acc. Chem. Res.* **2001**, *34*, 60–71. (c) Casado, C. M.; Cuadrado, I.; Moran, M.; Alonso, B.; Garcia, B.; Gonzalez, B.; Losada, J. *Coord. Chem. Rev.* **1999**, *185–6*, 53–79. (d) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26–34.

<sup>(17) (</sup>a) Kaifer, A. E. Eur. J. Inorg. Chem. 2007, 5015–5027. (b) Ong, W.; Gomez-Kaifer, M. Chem. Commun. 2004, 1677–1683. (c) Cuadrado, I.; Moran, M.; Casado, C. M.; Alonso, B.; Losada, J. Coord. Chem. Rev. 1999, 193–5, 395–445.

<sup>(18) (</sup>a) van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Rev.* **2002**, *102*, 3717–3756. (b) Kreiter, R.; Kleij, A. W.; Gebbink, R. J. M. K.; van Koten, G. *Top. Curr. Chem.* **2001**, *217*, 163–199. (c) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991–3031. (d) Oosterom, G. E.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1828–1849. (e) Lemo, J.; Heuze, K.; Astruc, D. *Chem. Commun.* **2007**, 4351–4353.

<sup>(19) (</sup>a) Dash, B. P.; Satapathy, R.; Maguire, J. A.; Hosmane, N. S. *Org. Lett.* **2008**, *10*, 2247–2250. (b) Dash, B. P.; Satapathy, R.; Gaillard, E. R.; Maguire, J. A.; Hosmane, N. S. *J. Am. Chem. Soc.* **2010**, *132*, 6578–6587, and references therein. (c) Yang, J.-X.; Tao, X.-T.; Yuan, C. X.; Yan, Y. X.; Wang, L.; Liu, Z.; Ren, Y.; Jiang, M. H. *J. Am. Chem. Soc.* **2005**, *127*, 3278–3279.

<sup>(20)</sup> Dash, B. P.; Satapathy, R.; Maguire, J. A.; Hosmane, N. S. Chem. Commun. 2009, 3267–3269.

<sup>(21) (</sup>a) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, Germany, 1996. (b) Grayson, S. M.; Frechet, J. M. *J. Chem. Rev.* **2001**, *101*, 3819–3867

<sup>(22)</sup> Cammidge, A. N.; King, A. S. H. Tetrahedron Lett. 2006, 47, 5569–5572.

<sup>(23)</sup> Lee, C.-H.; Yamamoto, T. Tetrahedron Lett. 2001, 42, 3993–3996.

synthesis of liquid crystalline and nonlinear optical materials as well as in a number of other areas. 24 The synthesis of the 1,3,5-triazine core based symmetrical compound 10, containing three cobaltabis(dicarbollide) clusters, is shown in Scheme 2. Similar to the procedure as described in Scheme 1, the synthesis of 10 was carried out using two different methods. In the first method, 2,4,6-tris(p-hydroxyphenyl)triazine 8 was synthesized from commercially available 4-cyanophenol via triflic acid-mediated cyclotrimerization, and then this was treated with 2. The ring-opening reaction took place in the presence of potassium carbonate, which led to the formation of 10 in 95% yield. In the second approach, 4-cyanophenol was first treated with 2 in the presence of potassium carbonate, and then compound 9 was formed.

Scheme 2. Synthesis of 10 via Trimerization of Cyano Derivatives

This was then treated with triflic acid in chloroform to produce 10 in about 75% yield.

After the synthesis of phenylene and triazine core based trimers containing three peripheral cobaltabis(dicarbollide) clusters was successfully carried out, we extended the study to make a phenylene core based trimer containing additional peripheral cobaltabis(dicarbollide) clusters. The synthesis of such a trimer, containing six cobaltabis(dicarbollides), is outlined in Scheme 3. The synthesis of trimer 13 was started from the commercially available 3,5-dihydroxyacetophenone 11. The nucleophilic ring-opening reaction of 2 in the presence of base and 11 led to the ketone 12 in quantitative vield. Then the ketone 12 underwent a silicon tetrachloride/ ethanol-mediated trimerization reaction to form the trimer 13, which contains six cobaltabis(dicarbollides).

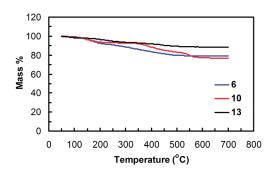
All compounds were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR, IR, and elemental analysis. The IR spectra of compounds containing cobaltabis(dicarbollide) clusters showed strong bands between 2550 and 2570 cm<sup>-1</sup> corresponding to  $\nu$ (B–H). For ketones **5** and **12** bands were observed at 1717 and 1737 cm<sup>-1</sup>, corresponding to  $\nu$ (C=O). The aromatic nitrile 9 showed a moderate band at 2233 that corresponds to  $\nu(C \equiv N)$ . The presence of cobaltabis(dicarbollide) clusters was also evident from the <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectra.

<sup>(24) (</sup>a) Wolff, J.; Siegler, F.; Matschiner, R.; Wortmann, R. Angew. Chem., Int. Ed. 2000, 39, 1436–1439. (b) Hirschberg, T. H. K. Ky.; Brunsveld, L.; Ramzi, A.; Vekemans, J. J. M.; Sijbesma, R.; Meijer, E. W. Nature 2000, 407, 167-170. (c) Acharya, S. N. G.; Gopalan, R. S.; Kulkarni, G. U.; Venkatesan, K.; Bhattacharya, S. Chem. Commun. 2000, 1351-1352. (d) Pohlers, G.; Sinta., J. C. S.; Brainard, R.; Pai, D. Chem. Mater. 1997, 9, 1353-1361. (e) Cherioux, F.; Maillotte, H.; Audebert, P.; Zyss, J. Chem. Commun. 1999, 2083-2084. (f) Brasselet, S.; Cherioux, F.; Audebert, P.; Zyss, J. Chem. Mater. 1999, 11, 1915-1920. (g) Janietz, D. J. Mater. Chem. 1998, 8, 265-274. (h) Goldmann, D.; Janietz, D.; Schmidt, C.; Wendorff, J. H. Liq. Cryst. 1998, 25, 711-719. (i) Malthete, J.; Leclercq, M.; Dvolaitzky, M.; Gabard, J.; Billard, J.; Pontikis, V.; Jacques, J. Mol. Cryst. Liq. Cryst. 1973, 23, 233-260. (j) Lim, J.; Mintzer, M. A.; Perez, L. M.; Simanek, E. E. Org. Lett. 2010, 12, 1148-1151. (k) Chouai, A.; Simanek, E. E. J. Org. Chem. 2008, 73, 2357-2366.

### Scheme 3. Synthesis of 13 via Trimerization of 12

Broad peaks between  $\delta$  3.5 and 4.3 ppm were observed in the  $^{1}H$ NMR spectra, which represent cluster C-H. Peaks observed at  $\delta$  46 and 53 ppm in the <sup>13</sup>C NMR spectra are due to the cluster carbons. The proton-decoupled <sup>11</sup>B NMR spectra also indicated the presence of cobaltabis(dicarbollides), and peaks were observed between  $\delta$  23 and -29 ppm. The NMR peak for the substituted B(8) boron atom of the cluster was observed around  $\delta$  23 ppm, which is in agreement with the literature. The presence of aliphatic polyether chains was observed by the presence of resonances between  $\delta$  3.5 and 4.4 ppm in the <sup>1</sup>H NMR, and peaks were also observed between  $\delta$  67 and 72 ppm in the  $^{13}$ C NMR spectra. Phenyl protons and carbons of phenylene and triazine cores also showed resonances in the appropriate region (see SI). Finally, the mass spectral data of all compounds confirmed their formation. The MALDI-TOF mass spectral data for trimers 6, 10, and 13 showed prominent peaks at m/z 1661.63  $[M^+-K]$ , 1665.01  $[M^+-K]$ , and 2976.15  $[M^+-3K+1]$  (see SI). The mass spectral data for compounds 6 and 10 were found to be identical for both synthetic approaches. Prominent peaks were observed for the molecular ion, indicating that the cyclic oxonium derivative 2 could be a useful synthetic building block for both convergent and divergent approaches of synthesizing symmetrical molecules. The MALDI-TOF spectra of compounds 6 and 10 are those obtained from the divergent synthetic approach, and they have been included in the SI. However, the yields of trimerization of keto and cyano derivatives, 5 and 9, were found to be slightly lower than what was found in the divergent approach.

**Thermal Properties.** Some unique properties of boron clusters and weakly coordinating carborane anions have been exploited for the synthesis of a variety of polymeric materials. These include thermally stable polymeric materials and ceramics. <sup>25</sup> light-emitting luminescent polymers. <sup>26</sup>



**Figure 2.** TGA curves of cobaltabis(dicarbollides) trimers under argon.

conducting organic polymers (COPs),<sup>6</sup> and coordination polymers.<sup>7,27</sup> Over the past few decades several groups have reported the incorporation of carboranes into polymeric backbones, using various well-established polymer linking processes.<sup>28</sup> In addition, a few carborane-siloxane elastomers, bearing the commercial names Dexsil and Ucarsil, have found specialized applications.<sup>29</sup> Recent studies on the thermal properties of compounds containing multiple orthocarborane clusters in our laboratory also led to the conclusion that incorporation of carborane units enhances thermal stability. 19b,20 Therefore, we were interested in the thermal properties of the trimers that contain multiple cobaltabis-(dicarbollide) clusters. TGA curves of trimers 6, 10, and 13 are compared in Figure 2. As can be seen, the thermal decomposition is not simple; they all maintain a constant mass until about 150 °C and have finished their mass loss by about 550 °C. The temperatures at which 10% mass loss occurred for 6, 10, and 13 were found to be 270, 380, and 470 °C, respectively. The 270 °C reported for 6 is not all that

<sup>(25) (</sup>a) Mark, A. F.; Kenneth, W. J. Mater. Chem. 2002, 12, 1301–1306. (b) Hideaki, K.; Koichi, O.; motokuni, I.; Toshiya, S.; Shigeki, K.; Isao, A. Chem. Mater. 2003, 15, 355–362. (c) Quan, Z.; Zuju, M.; Lizhong, Ni.; Jianding, C. J. Appl. Polym. Sci. 2007, 104, 2498–2503.

<sup>(26) (</sup>a) Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, *42*, 9238–9242. (b) Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, *42*, 2925–2930. (c) Peterson, J. J.; Simon, Y. C.; Coughlin, E. B.; Carter, K. R. *Chem. Commun.* **2009**, 4950–4952. (d) Nagata, Y.; Chujo, Y. *Macromolecules* **2008**, *41*, 2809–2813. (e) Sundararaman, A.; Victor, M.; Varughese, R.; Jakle, F. *J. Am. Chem. Soc.* **2005**, *127*, 13748–13749.

<sup>(27) (</sup>a) Westcott, A.; Whitford, N.; Michaele, J.; Hardie, M. J. *Inorg. Chem.* **2004**, *43*, 3663–3672. (b) Ahmad, R.; Dix, I.; Hardie, M. J. *Inorg. Chem.* **2003**, *42*, 2182–2184. (c) Ahmad, R.; Franken, A.; Kennedy, J. D.; Hardie, M. J. *Chem.*—*Eur. J.* **2004**, *10*, 2190–2198. (d) Ahmad, R.; Hardie, M. J. *Cryst. Growth Des.* **2003**, *3*, 493–499. (e) Cunha-Silva, L.; Westcott, A.; Whitford, N.; Hardie, M. J. *Cryst. Growth Des.* **2006**, *3*, 726–735.

<sup>(28) (</sup>a) Ichitani, M.; Yonezawa, K.; Okada, K.; Sugimoto, T. *Polym. J.* **1999**, *31*, 908–912. (b) Papetti, S.; Schaeffer, B. B.; Gray, A. P.; Heying, T. L. *J. Polym. Sci. Part A-1* **1996**, *4*, 1623–1636.

<sup>(29)</sup> Grimes, R. N. Carboranes; Academic Press: New York, 1970.

different from that found for the unsubstituted phenylene core (257 °C)<sup>19b</sup> and much less than the carborane-substituted phenylene cores.<sup>19b</sup> However, for all these trimers a very high residue weight percent was maintained even at 700 °C, which is about 79%, 76%, and 88% of the mass for trimers **6**, **10**, and **13**, respectively. This is most likely due to the high inorganic cobaltabis(dicarbollide) component.

#### Conclusion

Silicon tetrachloride- and triflic acid-mediated cyclotrimerization of cobaltabis(dicarbollide)-appended aromatic ketones and nitriles has been found to be an efficient method for the synthesis of phenylene and triazine core based thermally stable star-shaped molecules. The nucleophilic ring-opening reaction of zwitterionic [3,3'-Co(8-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] is also found to be suitable for both convergent and divergent approaches of making dendritic macromolecules. It is also found that compounds containing multiple cobaltabis(dicarbollides) exhibit only a 10-30% mass loss up to 700 °C. An increase in the number of cobaltabis(dicarbollides) in the molecule is found to enhance the thermal stability.

### **Experimental Section**

General Methods and Instrumentation. Reactions were generally performed under argon in oven-dried flasks. Solvents and reagents were added by syringes. Solvents were dried and distilled using standard procedures. Reagents were purchased and were used as received without further purification. All compounds were purified by column chromatography on silica gel (70–230 mesh, Aldrich). Yields of the products refer to analytically pure samples. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Fourier transform multinuclear NMR spectrometer at 500.13 and 125.75 MHz, respectively. Chemical shifts are reported relative to TMS ( ${}^{1}$ H:  $\delta = 0.00$  ppm) and CDCl<sub>3</sub> ( $^{13}$ C:  $\delta = 77.0$  ppm), and coupling constants are given in hertz. All <sup>13</sup>C spectra are proton-decoupled. <sup>11</sup>B NMR spectra were recorded at 64.2 and 160.5 MHz relative to BF<sub>3</sub>·Et<sub>2</sub>O. Infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer CHN analyzer 2400. Melting points were measured with a Mel-Temp II apparatus (Laboratory Devices, USA) and are uncorrected. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 analyzer at a heating rate of 5 °C/min under argon. Mass spectral analyses were performed with an Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer and a Waters O-TOF Ultima ES spectrometer.

Preparations and Analytical Data of Compounds. Ketone 5. 4-Hydroxyacetophenone 3 (175 mg, 1.29 mmol) was dissolved in 20 mL of acetonitrile. Then K<sub>2</sub>CO<sub>3</sub> (1.25 g, 9.03 mmol) and 2 (530 mg, 1.29 mmol) were added, and it was refluxed at 90 °C for 6 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 50-70% ethyl acetate in hexanes as the eluent to obtain 574 mg of pure compound 5 as a yellow solid, yield 76%. Melting point: > 250 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  7.97 (d, 2H, J = 7.0 Hz, Ar-H), 7.03 (d, 2H, J = 7.0 Hz, Ar-H), 4.21-4.20 (m, 4H,  $C_{cage}$ -H, O-C $H_2$ ), 4.16 (br s, 2H, O-C $H_2$ ), 3.83–3.81 (m, 2H, O-Č $H_2$ ), 3.64-3.63 (m, 2H, O-C $H_2$ ), 3.60-3.58 (m, 2H, O-C $H_2$ ), 2.54 (s, 3H,  $CH_3$ ). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125 MHz):  $\delta$  196.5 (C=O), 162.7 (Ar-C), 130.4 (Ar-C), 114.2 (Ar-C), 72.0 (O-CH<sub>2</sub>), 69.0 (O-CH<sub>2</sub>), 68.4 (O-CH<sub>2</sub>), 67.9 (O-CH<sub>2</sub>), 53.5 (C<sub>cage</sub>), 46.7 (C<sub>cage</sub>), 25.7 (CH<sub>3</sub>).  $^{11}$ B NMR (proton decoupled):  $\delta$  23.51 (1B), 4.59 (1B), 0.01 (1B), -2.70 (1B), -4.75 (2B), -7.66 (6B), -17.39 (2B),

-20.41 (3B), -28.48 (1B). IR (KBr): 3041, 2931, 2562 (B-H), 1717, 1671, 1600, 1254, 1097, 978, 836 cm<sup>-1</sup>. Anal. Calcd for C<sub>16</sub>H<sub>36</sub>B<sub>18</sub>CoKO<sub>4</sub>: C 32.85, H 6.20. Found: C 32.80, H 6.19. MALDI-TOF-MS (m/z): calcd 585.08, found 547.23 (M<sup>+</sup> - K + 1, 100%).

**Ketone 12.** 3,5-Dihydroxyacetophenone 11 (161 mg, 1.05 mmol) was dissolved in 25 mL of acetonitrile. Then K<sub>2</sub>CO<sub>3</sub> (1.75 g, 12.69 mmol) and 2 (870 mg, 2.11 mmol) were added, and the mixture was refluxed at 90 °C for 6 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with ethyl acetate to 5% methanol in ethyl acetate as the eluent to obtain 783 mg of pure compound 12 as a yellow solid, yield 71%. Melting point: >250 °C. <sup>1</sup>H NMR  $(CD_3CN, 500 \text{ MHz}): \delta 7.14 \text{ (d, 2H, } J = 2.25 \text{ Hz, Ar-}H), 6.79 \text{ (d, }H)$ 1H, J = 2.15 Hz, Ar-H), 4.18–4.17 (m, 4H C<sub>cage</sub>, 4H O-C $H_2$ ), 4.13 (br s, 4H, C<sub>cage</sub>-H), 3.83–3.81 (m, 4H, O-CH<sub>2</sub>), 3.68 (br s, 4H, O-C $H_2$ ), 3.61–3.60 (m, 4H, O-C $H_2$ ) 2.58 (s, 3H, C $H_3$ ). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125 MHz):  $\delta$  197.8 (C=O), 160.0 (Ar-C), 139.2 (Ar-C), 107.1 (Ar-C), 106.0 (Ar-C), 71.9 (O-CH<sub>2</sub>), 69.1 (O-CH<sub>2</sub>) CH<sub>2</sub>), 68.5 (O-CH<sub>2</sub>), 67.9 (O-CH<sub>2</sub>), 53.3 (C<sub>cage</sub>), 46.8 (C<sub>cage</sub>), 26.3 (CH<sub>3</sub>). <sup>11</sup>B NMR (proton decoupled): δ 23.75 (2B), 4.95 (2B), 0.11 (2B), -2.66 (2B), -5.06 (4B), -7.47 (12B), -17.42 (4B), -20.33 (6B), -28.21 (2B). IR (KBr): 3044, 2929, 2569 (B-H), 1737, 1595, 1443, 1095, 968 cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>64</sub>B<sub>36</sub>Co<sub>2</sub>O<sub>7</sub>K<sub>2</sub>: C 27.45, H 6.14. Found: C 27.43, H 6.12. MALDI-TOF-MS (m/z): calcd 1050.01, found 1041.86 (M<sup>+</sup> -BH + 1, 100%).

1,3,5-Tris(4-hydroxyphenyl)benzene, 4. 4-Hydroxyacetophenone (3) (1.0 g, 7.34 mmol) was dissolved in 30 mL of dry ethanol. Then SiCl<sub>4</sub> (4.2 mL, 36.73 mmol) was added to it at 0 °C. The mixture was stirred at 0 °C for 10 min and then at room temperature for 16 h. The reaction mixture was quenched with water and extracted with dichloromethane. The combined organic layer was dried over MgSO<sub>4</sub>. After evaporation of the solvent the residue was purified by silica gel column chromatography with 40% ethyl acetate in hexane as eluent to obtain 620 mg of pure compound 4 as a colorless solid, yield 71%. Melting point: 230 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz): δ 7.62 (s, 3H, Ar-H), 7.55 (d, 6H, J = 8.4 Hz, Ar-H), 6.92 (d, 6H, J = 8.4 Hz, Ar-H), 7.41 (br s, 3H, -OH). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125 MHz):  $\delta$  156.5 (Ar-C), 141.8 (Ar-C), 132.8 (Ar-C), 128.3 (Ar-C), 128.2 (Ar-C), 115.7 (Ar-C). Anal. Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>3</sub>: C 81.34, H 5.12. Found: C 81.31, H 5.15. ES-MS (m/z): calcd 354.39, found 355.1 ( $M^+ + 1$ , 100%).

**Trimer 6.** *Method A:* 1,3,5-Tris(4-hydroxyphenyl)benzene (4) (100 mg, 0.282 mmol) was dissolved in 10 mL of acetonitrile. Then K<sub>2</sub>CO<sub>3</sub> (584 mg, 4.23 mmol) and **2** (383 mg, 0.93 mmol) were added, and the mixture was refluxed at 90 °C for 6 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with ethyl acetate to 2% methanol in ethyl acetate as the eluent to obtain 422 mg of pure compound 6 as a yellow solid, yield 88%. Method B: Ketone 5 (460 mg, 0.84) mmol) was dissolved in 10 mL of dry ethanol. Then SiCl<sub>4</sub> (0.5 mL, 4.2 mmol) was added to it at 0 °C. It was stirred at 0 °C for 10 min and then stirred at room temperature for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate three times. The combined organic layer was dried over MgSO<sub>4</sub>. After evaporation of the solvent the residue was purified by silica gel column chromatography with ethyl acetate to 2% methanol in ethyl acetate as the eluent to obtain 350 mg of pure compound 6 as a yellow solid, yield 76%. Melting point: > 250 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  7.78 (s, 3H, Ar-H), 7.76–7.73 (m, 6H, Ar-H), 7.01–7.05 (m, 6H, Ar-H), 4.23–4.19 (m, 12H  $C_{cage}$ , 6H O-C $H_2$ ), 3.72–3.59 (m, 18H, O-C $H_2$ ). <sup>13</sup>C NMR (CD<sub>3</sub>ČN, 125 MHz): δ 158.7 (Ar-C), 141.6 (Ar-C), 133.5 (Ar-C), 128.4 (Ar-C), 123.3 (Ar-C), 114.9 (Ar-C), 71.8 (O-CH<sub>2</sub>), 69.2 (O-CH<sub>2</sub>), 68.6 (O-CH<sub>2</sub>), 67.6 (O-CH<sub>2</sub>), 53.5 (C<sub>cage</sub>), 46.7  $(C_{cage})$ . <sup>11</sup>B NMR (proton decoupled):  $\delta$  23.6 (3B), 4.7 (3B), 0.03 (3B), -2.46 (3B), -4.82 (6B), -7.54 (18B), -17.30 (6B), -20.27 (9B), -28.45 (3B). IR (KBr): 3044, 2974, 2560 (B-H), 1604, 1509, 1399, 1244, 1095, 828 cm<sup>-1</sup>. Anal. Calcd for  $C_{48}H_{102}-B_{54}Co_3K_3O_9$ : C 33.89, H 6.04. Found: C 33.84, H 6.01. MALDITOF-MS (m/z): calcd 1701.20, found 1661.63 (M<sup>+</sup> - K, 100%), 1212.91 (M<sup>+</sup> -  $C_8H_{27}B_{18}CoK_2O_2 + 1$ ).

Trimer 13. Ketone 12 (450 mg, 0.426 mmol) was dissolved in 8 mL of dry ethanol. Then SiCl<sub>4</sub> (0.5 mL, 4.26 mmol) was added to it at 0 °C. The mixture was stirred at 0 °C for 10 min and then at room temperature for 24 h. The reaction mixture was quenched with water and then extracted with ethyl acetate three times. The combined organic layer was dried over MgSO<sub>4</sub>. After evaporation of the solvent the residue was purified by silica gel column chromatography with ethyl acetate to 10% methanol in ethyl acetate as eluent to obtain 250 mg of pure compound 13 as yellow solid, yield 56%. Melting point: >250 °C. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz):  $\delta$  6.76 (s, 3H, Ar-H), 6.66 (br, 3H, Ar-H) 6.57 (br, 3H, Ar-H), 6.49 (br, 3H, Ar-H), 4.13 (br, 24H C<sub>cage</sub>,  $12H \text{ O-C}H_2$ ), 3.88-3.81 (m, 12H,  $O-CH_2$ ), 3.73-3.67 (m, 24H, O-C $H_2$ ). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz):  $\delta$  158.8 (Ar-C), 149.1 (Ar-C), 140.4 (Ar-C), 125.6 (Ar-C), 124.1 (Ar-C), 107.6 (Ar-C), 71.7 (O- $CH_2$ ), 69.4 (O- $CH_2$ ), 68.7 (O- $CH_2$ ), 67.5 (O- $CH_2$ ), 53.1 ( $C_{cage}$ ), 46.3 ( $C_{cage}$ ). <sup>11</sup>B NMR (proton decoupled):  $\delta$  23.0 (8B), 4.43 (6B), -7.18 (66B), -17.23 (30B). IR (KBr): 3044, 2930, 2563 (B-H), 1607, 1453, 1401, 1250, 1160 cm<sup>-1</sup>. Anal. Calcd for C<sub>72</sub>H<sub>186</sub>B<sub>108</sub>Co<sub>6</sub>K<sub>6</sub>O<sub>18</sub>: C 27.93, H 6.06. Found: C 27.91, H 6.05. MALDI-TOF-MS (m/z): calcd 3096.01, found 2976.15  $(M^+ - 3K + 1, 100\%).$ 

Comopund 9. 4-Cyanophenol 7 (50 mg, 0.42 mmol) was dissolved in 10 mL of acetonitrile. Then K<sub>2</sub>CO<sub>3</sub> (405 mg, 2.94 mmol) and 2 (173 mg, 0.42 mmol) were added, and the mixture was refluxed at 90 °C for 5 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 50-70% ethyl acetate in hexane as the eluent to obtain 200 mg of pure compound 9 as a yellow solid, yield 84%. Melting point: > 250 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  7.68 (d, 2H, J = 7.0 Hz, Ar-H, 7.0 (d, 2H, J = 7.0 Hz, Ar-H), 4.22 (br s, 2H,  $C_{cage}$ -H), 4.20-4.18 (m, 2H, O-CH<sub>2</sub>), 4.15 (br s, 2H,  $C_{cage}$ -H), 3.83–3.81 (m, 2H, O-C $H_2$ ), 3.64–3.63 (m, 2H, O-C $H_2$ ), 3.59–3.58 (m, 2H, O-C $H_2$ ).  $^{13}$ C NMR (CD<sub>3</sub>CN, 125 MHz):  $\delta$ 162.3 (Ar- $\dot{C}$ ), 134.1 (Ar- $\dot{C}$ ), 119.0 (Ar- $\dot{C}$ ), 115.4 (C=N), 103.5 (Ar-C), 72.0 (O-CH<sub>2</sub>), 68.9 (O-CH<sub>2</sub>), 68.5 (O-CH<sub>2</sub>), 68.0 (O-CH<sub>2</sub>), 53.5 ( $C_{cage}$ ), 46.7 ( $C_{cage}$ ). <sup>11</sup>B NMR (proton decoupled, 160.5 MHz):  $\delta$  23.53 (1B), 4.52 (1B), 0.02 (1B), -2.65 (1B), -4.83 (2B), -7.48 (2B), -7.93 (2B), -8.76 (2B), -17.42 (2B), -20.38(2B), -22.22 (1B), -28.60 (1B). IR (KBr): 3042, 2930, 2566 (B-H), 2233, 1604, 1507, 1209, 1097 cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>33</sub>B<sub>18</sub>CoKO<sub>3</sub>N: C 31.72, H 5.86. Found: C 31.70, H 5.84. MALDI-TOF-MS (m/z): calcd 568.05, found 528.96 (M<sup>+</sup> -K + 1, 100%).

**2,4,6-Tris(p-hydroxyphenyl)triazine, 8.** 4-Cyanophenol (7) (500 mg, 4.197 mmol) was dissolved in 10 mL of dry chloroform. Then CF<sub>3</sub>SO<sub>3</sub>H (1.9 mL, 20.98 mmol) was added to it at 0 °C. The mixture was stirred at 0 °C for 10 min and then at room temperature for 24 h. The reaction mixture was quenched with water containing a small amount of NH<sub>4</sub>OH. Then the reaction

mixture was filtered over a cotton plug, and the residue was dissolved in acetone and then recrystallized from acetone to obtain 400 mg of pure compound **8** as a colorless solid, yield 80%. Melting point: >250 °C. <sup>1</sup>H NMR (acetone- $d_6$ , 500 MHz):  $\delta$  8.67 (d, 6H, J = 7.0 Hz, Ar-H), 7.07 (d, 6H, J = 7.0 Hz, Ar-H), 7.67 (br s, 3H, -OH). <sup>13</sup>C NMR (acetone- $d_6$ , 125 MHz):  $\delta$  170.6 (C=N), 161.6 (Ar-C), 130.7 (Ar-C), 127.7 (Ar-C), 115.4 (Ar-C). Anal. Calcd for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>: C 70.58, H 4.23, N 11.76. Found: C 70.53, H 4.21, N 11.79. ES-MS (m/z): calcd. 357.36, found 358.2 (M<sup>+</sup> + 1, 100%).

Compound 10. Method A: Compound 8 (100 mg, 0.279 mmol) was dissolved in 10 mL of dry acetone. Then K<sub>2</sub>CO<sub>3</sub> (577.5 mg, 4.18 mmol) and 2 (378 mg, 0.92 mmol) were added, and the mixture was refluxed at 70 °C for 7 h. Then the reaction mixture was filtered through a cotton plug. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 5% methanol in ethyl acetate as the eluent to obtain 452 mg of pure compound 10 as a yellow solid, yield 95%. Method B: Compound 9 (170 mg, 0.32 mmol) was dissolved in 5 mL of chloroform. Then CF<sub>3</sub>SO<sub>3</sub>H (0.3 mL, 3.4 mmol) was added to it. The mixture was then stirred at room temperature for 20 h and then at 40 °C for 2 h. The reaction mixture was quenched with water containing a small amount of NH<sub>4</sub>OH. Then it was extracted with about 150 mL of dichloromethane three times. The combined organic layer was dried over MgSO<sub>4</sub>. After evaporation of the solvent the residue was purified by silica gel column chromatography with ethyl acetate to 5% methanol in ethyl acetate as the eluent to obtain 118 mg of pure compound 10 as yellow solid, yield 76%. Melting point: > 250 °C. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz):  $\delta$  8.73 (d, 6H, J = 8.9Hz, Ar-H), 7.18 (d, 6H, J = 9.0 Hz, Ar-H), 4.30–4.28 (br, 8H, C<sub>cage</sub>-H, O-CH<sub>2</sub>), 4.16 (br s, 6H, C<sub>cage</sub>-H), 4.09-4.05 (m, 8H, O- $\dot{C}H_2$ ), 3.94–3.92 (m, 8H, O- $\dot{C}H_2$ ), 3.75–3.57 (m, 6H, O- $\dot{C}H_2$ ). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz):  $\delta$  170.6 (C=N), 162.5 (Ar-C), 130.4 (Ar-C), 128.9 (Ar-C), 114.3 (Ar-C), 71.9 (O-CH<sub>2</sub>), 69.2 (O-CH<sub>2</sub>), 68.3 (O-CH<sub>2</sub>), 67.5 (O-CH<sub>2</sub>), 53.0 ( $C_{cage}$ ), 46.9 ( $C_{cage}$ ). <sup>11</sup>B NMR (proton decoupled):  $\delta$  23.72 (3B), 5.43 (3B), 0.54 (6B), -6.99 (6B), -17.23 (24B), -19.97 (12B). IR (KBr): 3042, 2925, 2551 (B-H), 1605, 1508, 1367, 1255, 1206, 965 cm $^{1-}$ . Anal. Calcd for  $C_{45}H_{99}B_{54}N_3Co_3K_3O_9$ : C 31.72, H 5.86, N 2.47. Found: C 31.70, H 5.85 N 2.50. MAL-DI-TOF-MS (m/z): calcd 1704.17, found 1665.01  $(M^+ - K,$ 100%), 1324.13 (M<sup>+</sup> – C<sub>4</sub>H<sub>21</sub>B<sub>18</sub>CoKO – 1).

Acknowledgment. We thank Dr. Amartya Chakrabarti for assistance during TGA studies. This work was supported by grants from the National Science Foundation (CHE-0906179 and CHE-0840504), the Robert A. Welch Foundation (N-1322), the Alexander von Humboldt Foundation, and NIU Inaugural Board of Trustees Professorship Award.

**Supporting Information Available:** NMR and MALDI-TOF mass spectra of the compounds prepared in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.