J|A|C|S
ARTICLES

Organometallic Dendrimers Based on (Tetraphenylcyclobutadiene)cyclopentadienylcobalt Modules

Shane M. Waybright, Kanika McAlpine, Matthew Laskoski, Mark D. Smith, and
Uwe H. F. Bunz*

Contribution from the Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208

Received April 8, 2002

Abstract: The synthesis and characterization of novel organometallic polyphenylene dendrimers containing 24 or 44 phenyl rings and one cyclobutadiene(cyclopentadienyl)cobalt unit is reported. The dendrimers are made by the convergent $CpCo(CO)_2$-mediated dimerization of di- or tetraethynyltolanes followed by a divergent core extension utilizing tetraphenylcyclopentadienone. The obtained dendrimers are air and water stable, soluble materials that show interesting differences in their hydrodynamic properties as evidenced by gel permeation chromatography. Scanning pulse voltammetry in solution shows that the dendrimers are oxidized at potentials ranging from 0.8 to 0.83 V. The more sterically encumbered the dendrimer, the higher its oxidation potential, that is, the more difficult oxidation is.

Introduction

Dendritic molecules have attracted attention because of their exciting structures and carefully tailored properties;[1] polyphenylene dendrimers have been introduced by Müllen et al., who reported the reaction of alkynylated aromatic and nonaromatic cores with tetraphenylcyclopentadienone and its functionalized derivatives.[2] This straightforward, powerful approach has allowed the assembly of numerous polyphenylene dendrimers, some of which give large graphitic disks upon oxidative ring closure. Polyphenylene dendrimers are monodisperse rigid macromolecules of defined shape with significant internal voids. They are attractive in advanced sensing schemes.[3] While *organic* polyphenylene dendrimers have been reported by the MPI group, polyphenylene dendrimers with a central electroactive organometallic[4] core are not described to our knowledge.

The synthesis of such organometallic polyphenylene dendrimers should be facile if terminally alkynylated tetraphenylcyclobutadiene(cyclopentadienyl)cobalt complexes were available.[5] Their proposed reaction with tetraphenylcyclopentadienone should furnish organometallic polyphenylene dendrimers. We herein describe the synthetic scheme to and some interesting properties of simple cyclobutadiene(cyclopentadienyl)cobalt centered polyphenylene dendrimers.

Results and Discussion

Syntheses. The synthetic sequence starts out with the preparation of the prerequisite diarylalkynes **2b**, **4b**, **6b**, and **8b** (Scheme 1). While these materials have been described in the literature,[2,3] a simplified synthetic access was developed. Acetylene gas reacts with **1**, **3**, **5**, or **7** under standard Pd-catalysis to give the intermediate di- and tetrabromo-(diphenylacetylene)s **2a**, **4a**, **6a**, and **8a**. Replacement of the iodide substituents by acetylene is facile for these substrates, and yields of the intermediates range from 75 to 99%. The yield of the dimerization products was highest if the loading of catalyst was low (0.1 mol % $[(Ph_3P)_2PdCl_2]$).[6c] Subsequent coupling of the intermediates to tri(isopropylsilyl)acetylene under standard conditions makes the triynes **2b**, **4b**, and **6b** and the pentayne **8b** accessible in yields between 33 and 86% for both coupling steps. The second coupling replaces the aromatic bromide by tri(isopropylsilyl)acetylene and is performed in triethylamine as solvent. A 10-fold higher catalyst loading (1 mol % $[(Ph_3P)_2PdCl_2]$) at elevated temperatures is necessary to overcome the decreased reactivity of the aromatic bromides. Triethylamine is the base and solvent of choice; while piperidine is excellent as base in the Heck−Cassar−Sonogashira−Hagihara

---

* Address correspondence to this author. E-mail: Bunz@mail.chem.sc.edu.

(1) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem.* **1990**, *29*, 138. Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402. Smith, D. K.; Diederich, F. *Chem. Eur. J.* **1998**, *4*, 1353. Archut, A.; Vögtle, F. *Chem. Soc. Rev.* **1998**, *27*, 233. Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665. Grayson, S. K.; Frechet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819. Gorman, C. B.; Smith, J. C. *Acc. Chem. Res.* **2001**, *34*, 60.

(2) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267. Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747. Ito, S.; Herwig, P. T.; Böhme, T.; Rabe, J. P.; Rettig, W.; Müllen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7698. Dötz, F.; Brand, J. D.; Ito, S.; Gherghel, L.; Müllen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7707. Weil, T.; Wiesler, U. M.; Herrmann, A.; Bauer, R.; Hofkens, J.; De Schryver, F. C.; Müllen, K. *J. Am. Chem. Soc.* **2001**, *123*, 8101. Müller, M.; Kübel, C.; Müllen, K. *Chem. Eur. J.* **1998**, *4*, 2099.

(3) Schlupp, M.; Weil, T.; Berresheim, A. J.; Wiesler, U. M.; Bargon, J.; Müllen, K. *Angew. Chem.* **2001**, *40*, 4011. Vossmeyer, T.; Guse, B.; Besnard, I.; Bauer, R. E.; Müllen, K.; Yasuda, A. *Adv. Mater.* **2002**, *14*, 238.

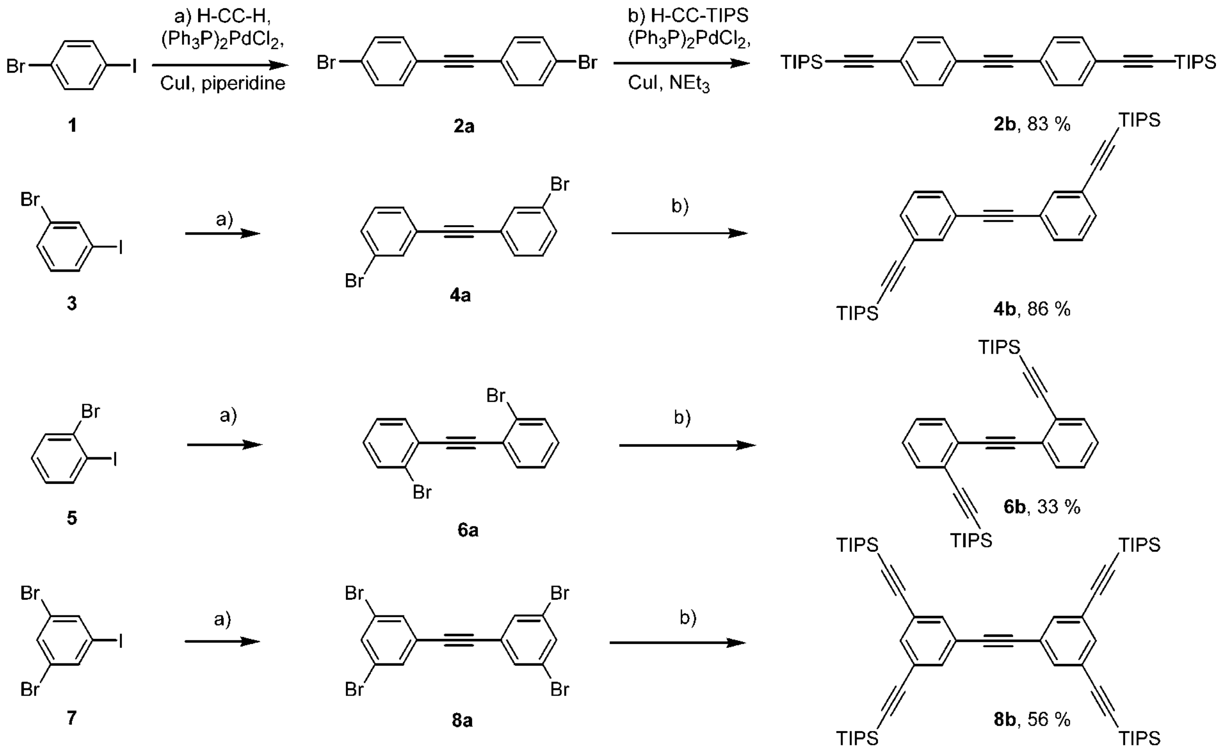
(4) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991. Astruc, D. *Acc. Chem. Res.* **2000**, *33*, 287. Astruc, D.; Blais, J. C.; Cloutet, E.; Djakovitch, L.; Rigaut, S.; Ruiz, J.; Sartor, V.; Valerio, C. *Top. Curr. Chem.* **2000**, *210*, 299.

(5) Bunz, U. H. F. *Top. Curr. Chem.* **1999**, *201*, 131. Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 131.

(6) (a) Li, C. J.; Slaven, W. T.; John, V. T.; Banerjee, S. *Chem. Commun.* **1997**, 1569. Li, C. J.; Slaven, W. T.; Chen, Y. P.; John, V. T.; Rachakonda, S. H. *Chem. Commun.* **1998**, 1351. (b) Iyoda, M.; Vorasingha, A.; Kuwatani, Y.; Yoshida, M. *Tetrahedron Lett.* **1998**, *39*, 4701. (c) Wilson, J. N.; Waybright, S. M.; McAlpine, K.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, ASAP.

10.1021/ja026462p CCC: $22.00

Scheme 1



coupling of aromatic *iodides*,[7] it gave less satisfying results in the substitution of bromides **2a**, **4a**, **6a**, and **8a**.

The reaction of disubstituted alkynes with cyclopentadienyl(dicarbonyl)cobalt ($CpCo(CO)_2$) grants facile access to functionalized cyclobutadiene complexes.[8] Yields of this dimerization step are high and can exceed 90% in the diarylalkynes or TMS-protected acetylenes. The phenyleneethynylenes **2b**, **4b**, **6b**, and **8b** are attractive because they contain two different types of alkynes. The outer ones are protected by the bulky triisopropylsilyl groups and should show negligible reactivity toward $CpCo(CO)_2$, while the inner ones, the diarylalkynes, should partake in the dimerization. Reaction of **2b** with $CpCo(CO)_2$ in boiling decane furnished the cyclobutadiene complex **9** in 75% yield (Scheme 2) after removal of the triisopropylsilyl groups with tetrabutylammonium fluoride. Side products that could be traced to the reaction of the triisopropylsilyl-protected alkynes with $CpCo(CO)_2$ were not detected, suggesting clean reaction of the di*aryl*alkyne unit.

Michl et al.[9] dimerized 4,4′-dibromotolane and performed Heck−Cassar−Sonogashira−Hagihara alkynylation of the intermediate [tetrakis(bromophenyl)cyclobutadiene]cyclopentadienylcobalt. They had obtained **9**, albeit in lower yield. Encouraged by the smooth reaction of **2b** with $CpCo(CO)_2$, the triyne **4b** was reacted under similar conditions to give the cyclobutadiene complex **10** in 24% yield. The byproduct was a dark brown mass of undefined structure and separated from **10** by column chromatography. If the alkyne groups are *ortho*-positioned with respect to each other, as in **6b**, reaction with $CpCo(CO)_2$ is unsuccessful and the starting material is reisolated after chromatography. It was possible to dimerize the pentayne **8b**; however, the cyclobutadiene complex **12** was isolated in only 12% yield after deprotection with tetrabutylammonium fluoride and repeated chromatography. Because of the facile access to the precursor pentayne **8b**, the low yield of the complex **12** did not prohibit the exploration of its reactivity. The decreasing yield in the dimerization reactions can be explained by the increasing steric encumbrance of the utilized diarylalkyne. The least encumbered alkyne, **2b**, gives the highest yields, while the bulky **6b** does not undergo the dimerization reaction at all. The steric bulk of **6b** makes it completely unreactive and it does not undergo cobalt mediated [2 + 2 + 2] cycloaddition reported by Vollhardt[10] to occur for the *parent* triyne **6**, void of the triisopropylsilyl groups.

The cyclobutadiene complexes **9**, **10**, and **12** are stable to air and light, are soluble in common organic solvents, and can be manipulated without problems. Diels−Alder reaction of **9**, **10**, and **12** with an excess of tetraphenylcyclopentadienone (Scheme 2) in boiling decaline furnished the organometallic dendrimers **13**−**15** in good-to-excellent yields (63−91%) as yellow powders after crystallization or chromatography. The ^1H NMR spectra of the products of the Diels−Alder reaction did not show the presence of terminal alkyne protons. Instead, in the aromatic region (Figure 1) **13** and **14** show a diagnostic singlet of H_a at $\delta = 7.63$ (4H, **13**), 7.63 (4H, **14**) that integrate to four protons and represents the former alkyne protons. In **15** this diagnostic singlet is not visible at ambient temperature. All of its NMR signals, including that of the Cp-ring, are significantly upfield shifted and broadened. This effect must be a consequence of the high steric pressure the 44 benzene rings exert, indicating a conformation in which face-to-face interactions of the arenes

---

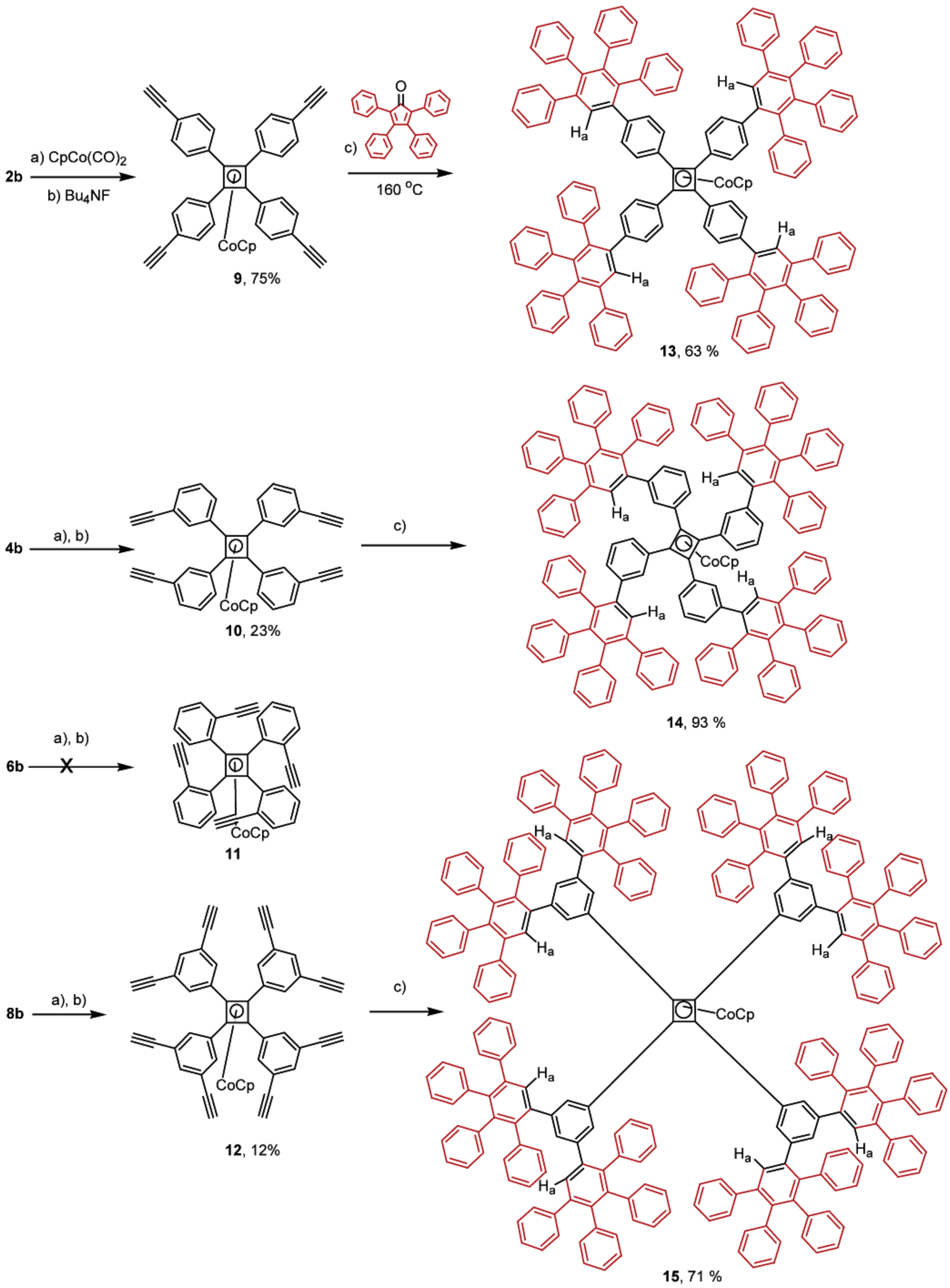
(7) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998.

(8) Efraty, A. *Chem. Rev.* **1977**, *77*, 691. Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590. Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem.* **1979**, *18*, 409.

(9) Harrison, R. M.; Brotin, T.; Noll, B. C.; Michl, J. *Organometallics* **1997**, *16*, 3401.

(10) Diercks, R.; Vollhardt, K. P. C. *Angew. Chem.* **1986**, *25*, 266. Eickmeier, C.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem.* **1997**, *36*, 2103.

Scheme 2


2b
a) CpCo(CO)2
b) Bu4NF
CoCp
9, 75%
c)
O
160 °C
Ha
CoCp
13, 63 %
4b
a), b)
CoCp
10, 23%
c)
Ha
CoCp
14, 93 %
6b
a), b)
CoCp
11
8b
a), b)
CoCp
12, 12%
c)
Ha
CoCp
15, 71 %

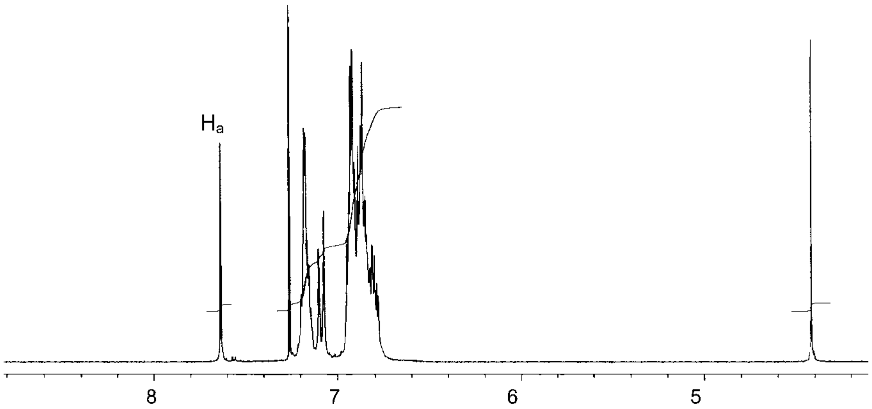


Figure 1. ^{1}H NMR spectrum of **13**. At δ 7.62 the unique singlet of H_a (part of the pentaphenylbenzene moiety) is visible. The alkyne resonance has disappeared. At δ 4.42 the singlet of the cyclopentadienyl ring is recorded. The signal at δ 7.23 is due to residual $CHCl_3$ in the solvent $CDCl_3$.

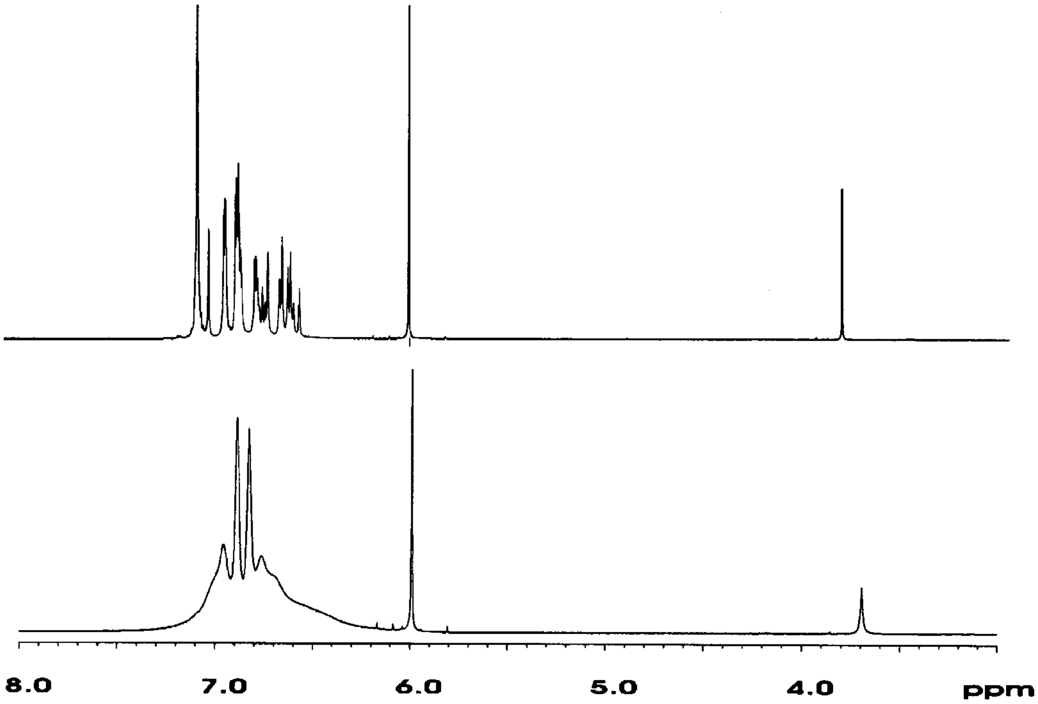


Figure 2. Variable temperature ^{1}H NMR spectrum of **15** taken at 25 °C (bottom) and at 115 °C (top) in tetrachloroethane d-2 (δ 6.00). At δ 6.98 (upper trace, small singlet) the signal of the H_a protons is visible. The most upfield shifted, unresolved triplet (δ 6.53) represents the four unique *para* protons of the innermost phenyl rings. The other resonances give the correct integration but cannot be assigned unequivocally. To higher field the distinct singlet of the Cp-ring is observed.

are enforced.[11] In Figure 2, the ^{1}H NMR spectra of **15** at 25 °C and at 115 °C are shown. While at ambient temperature the resonances are unresolved, at 115 °C a well-resolved spectrum is obtained, suggesting the free rotation of all benzene rings on the NMR time scale. The signal of the protons H_a in **15** can now be identified at $\delta = 6.98$, and a small unresolved triplet at $\delta = 6.53$ is assigned to the four unique *para* protons of the innermost benzene rings. The temperature dependence of the ^{1}H NMR spectra is consistent with the high steric pressure that the crowding of phenyl groups causes. The ^{1}H NMR and ^{13}C NMR spectra and other analytical data of the Diels−Alder adducts support smooth formation of the dendrimers **13**−**15**.

Properties and Structures of 9−15. To obtain proof for the structure of the cyclobutadiene complexes, we grew a single crystalline specimen of **9** from dichloromethane. An ORTEP representation is shown in Figure 3.[12] As expected, the four phenyl rings are twisted with respect to each other (Table 1). The propeller-shaped conformation of **9** is similar to that observed for the parent (tetraphenylcyclobutadiene)cyclopentadienylcobalt. The twist between the phenyl rings and the cyclobutadiene core is significant and ranges from 27 to 42°,[6,13] while the bond angles and bond lengths are in excellent agreement with reported values for cyclobutadiene complexes.[14]

---

(11) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525. Hunter, C. A. *Angew. Chem.* **1993**, *32*, 1584.

(12) Crystallographic data for **9**: C_{41} H_{25} Co; formula wt 576.54, $T = 180$ K, $l = 0.711$ Å; *orthorombic, Pbca*, $a = 11.1151(5)$ Å, $b = 20.7398(10)$ Å, $c = 25.8240(13)$ Å, $\alpha = \beta = \gamma = 90°$; $V = 5953.1(5)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 1.287$ g cm^{-3}; absorption coefficient = 0.604 mm^{-1}; crystal size 0.72 × 0.11 × 0.08 mm^3; $-9 \le h \le 13$, $-22 \le k \le 24$, $-30 \le l \le 30$; reflections collected 33 799, independent reflections 5272 [R(int) = 0.0790]; semiempirical absorption correction; refinement method: Full-matrix least-squares on F^2; $R_1 = 0.0479$, $wR_2 = 0.1025$; largest diffraction peak and hole: 0.342 and −0.323 e·Å^{-3}.

(13) Rausch, M. D.; Westover, G. F.; Mintz, E.; Reisner, G. M.; Bernal, I.; Clearfield, A.; Troup, J. M. *Inorg. Chem.* **1979**, *18*, 2605.

(14) Bunz, U. H. F.; Enkelmann, V. *Organometallics* **1994**, *13*, 3823.

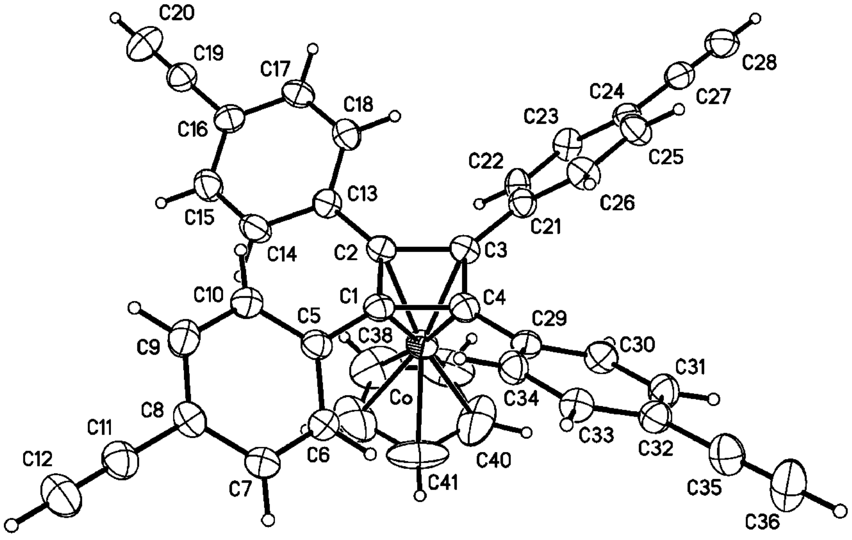


Figure 3. ORTEP of tetraalkynyated cyclobutadiene complex **9**.

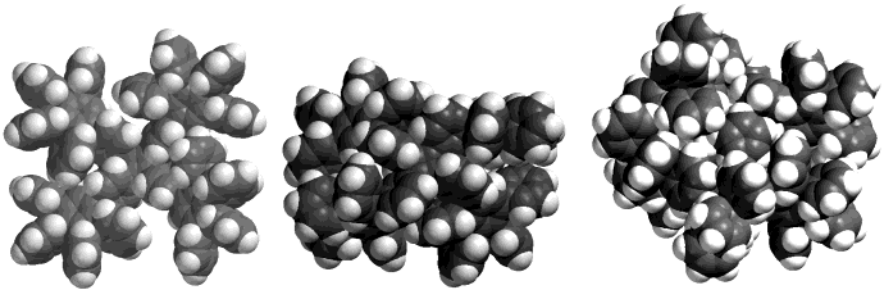


Figure 4. Space-filling representations of complexes **13**, **14**, and **15**. The structures were obtained utilizing semiempirical PM3 quantum chemical calculations. For **14** and **15** it is not clear if the represented structures are local minima or the global minimum. For the conformationally rigid **13** the global minimum is probably represented correctly.

Table 1. Interplanar Angles (°) of the Phenyl Rings and the Cyclobutadiene Core

	{C1···C4}	{C5···C10}	{C13···C18}	{C21···C26}
{C5···C10}	36.0			
{C13···C18}	27.5	45.1		
{C21···C26}	42.2	78.2	48.9	
{C29···C34}	30.7	46.2	58.1	49.0

Table 2. GPC Data for Complexes **13**, **14**, and **15**

complex	formula weight (FW)[a]	M_n[a]	M_w[a]	ratio M_n/FW	M_w/M_n	retention time[b]
13	2000	1490	1600	0.745	1.07	8.52
14	2000	1250	1320	0.625	1.06	8.63
15	3522	1820	1860	0.517	1.02	8.45

[a] Units in g/mol. [b] Time in min.

Unfortunately, attempts to grow single crystalline specimens from the other cyclobutadiene complexes or the Diels−Alder adducts **13**−**15** were unsuccessful and only powders were obtained.

We performed powder X-ray diffraction upon "as obtained" samples of dendrimer **13**; the material was amorphous. According to differential scanning calorimetry (DSC), **13** undergoes an irreversible exothermic phase transition at 319 °C (22.3 kcal mol^{-1}). No melting is observed up to 350 °C. Upon cooling, no endotherm is recorded in the DSC. Bulk samples of **13** heated to >320 °C are not amorphous but show a distinct but not interpretable powder XRD pattern. When the annealed material is dissolved in dichloromethane and the solvent is removed, the amorphous form of **13** is obtained again. Compared to the heat of fusion of benzene (2.53 kcal mol^{-1}), this seemingly large exotherm might be explained by the (possibly cooperative) ordering of the 24 benzene rings of the dendrimer **13** in the solid state. The *meta*-dendrimer **14** is microcrystalline at room temperature and shows two endothermic transitions at 291 (13.8 kcal mol^{-1}) and 331 °C (2.4 kcal mol^{-1}, melting). Its powder diffraction pattern is complex and likewise not useful for structure elucidation.

The molecular size of the *para* (**13**), *meta* (**14**), and double *meta* (**15**) Diels−Alder adducts (Figure 4) was investigated by gel permeation chromatography (GPC, Figure 5). All polydispersities (M_w/M_n) were between 1.02 and 1.07, giving credibility to the monodisperse nature of the dendrimers (Table 2). Both **13** and **14** have a formula weight of 2000 Da and **15** has a formula weight of 3522 Da. Comparing isomeric complexes **13** and **14**, **14** has a longer retention time than **13**, indicating that the *para* complex **13** has a *higher* hydrodynamic volume than the *meta* complex **14**. Space-filling models (Figure 4) show that the rigid dendrimer **13** adopts a more extended structure than **14** and thus features a higher hydrodynamic volume. Interestingly, the molecular weights obtained by GPC (Table 2) for **13**−**15** are underestimated by a factor that ranges from 1.3 to 1.9; the systematic deviation in the measurements is larger the more compact the dendrimer is. It is remarkable that **13** and **14** can be distinguished so clearly by GPC and that the difference in their hydrodynamic volumes is so distinct. These

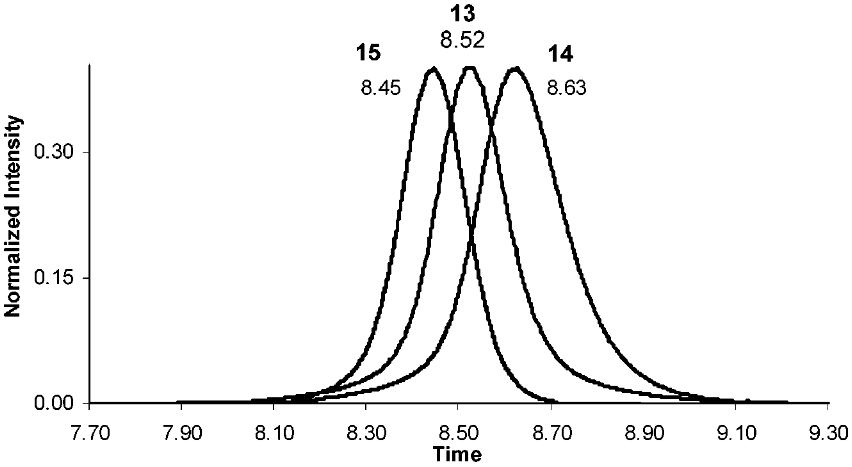


Figure 5. GPC chromatogram of complexes **13**, **14**, and **15**.

results corroborate observations by Shimizu[15] and McGrath[16] who demonstrated that more extended oligomers/dendrimers have significantly greater hydrodynamic volumes than less extended ones.

Model studies of encapsulated transition-metal complexes suggest[17] that the local surrounding of a metal significantly influences its electron-transfer properties and oxidation potential. The CpCo-ligated cyclobutadiene complexes **13**−**15** are electroactive[18] and undergo oxidation into their 17e cations. We performed scanning pulse voltammetry upon the complexes **13**−**15** and discovered a small but significant variation in their oxidation potential. While **13** is oxidized at 0.80 V in a differential pulse voltammetry experiment (ferrocene standard, nitrobenzene solvent), its *meta*-isomer **14** is oxidized at 0.82 V, and the larger crowded dendrimer **15** oxidizes at 0.83 V. These results suggest that oxidation is slightly more difficult in the more compact, enshrouded dendrimers where the benzene rings act as an insulating cover. The effects are not dramatic in solution, and in future we plan to investigate thin films of **13**−**15** electrochemically.

Conclusions

An access to novel organometallic dendrimers with cyclobutadiene cores has been developed. The combination of Pd-catalyzed couplings, cobalt-mediated [2 + 2] cycloadditions, and Diels−Alder chemistry allows the synthesis of **13**−**15**. The pinnacle of the synthetic effort is the high selectivity of the cyclobutadiene formation of **2b**, **4b**, and **8b**; $CpCo(CO)_2$ leaves TIPS-substituted alkynes untouched, and only the sterically less encumbered diarylalkyne units dimerize into the desired cyclobutadiene complexes. Desilylation and reaction with tetraphenylcyclopentadienone leads to organometallic dendrimers **13**−**15** with a cyclobutadiene(cyclopentadienyl)cobalt *core*. With the facile chemistry developed here, it should be possible to assemble larger nanoscale organometallic objects entirely composed of cyclobutadiene complexes and phenyl rings. Particularly, the functional complex **9** is an excellent starting point because it is available in multigram quantities. These organometallic dendrimers will show novel nanoscale structural and electrochemical properties.

Acknowledgment. We thank the University of South Carolina, the USC Nanocenter, and the National Science Foundation for support (CAREER CHE 9981765) of this project and Dr. K. Stitzer and Prof. H.-C. zur Loye for help with the powder diffraction experiments. U.H.F.B. is Camille and Henry Dreyfus Teacher Scholar.

Supporting Information Available: Experimental procedures, detailed spectroscopic characterization, and crystallographic information files (CIF) are available free of charge via the Internet at http://pubs.acs.org.

JA026462P

---

(15) Choi, D. S.; Chong, Y. S.; Whitehead, D.; Shimizu, K. D. *Org. Lett.* **2001**, *3*, 3757.

(16) Li, S.; McGrath, D. V. *J. Am. Chem. Soc.* **2000**, *122*, 6795.

(17) (a) Dandliker, P. J.; Diederich, F.; Gross, M.; Knobler, C. B.; Louati, A.; Sanford, E. M. *Angew. Chem.* **1994**, *33*, 1739. Dandliker, P. J.; Diederich, F.; Giselbrecht, J.-P.; Gross, M. *Angew. Chem.* **1995**, *34*, 2725. Dandliker, P. J.; Diedrich, F.; Zing, A.; Gisselbrecht, J.-P.; Gross, M.; Louati, A.; Sanford, E. *Helv. Chim. Acta* **1997**, *80*, 1773. (b) Cameron, C. S.; Gorman C. B. *Adv. Mater.* **2002**, *12*, 17.

(18) Geiger, W. E.; Kelly, R. S. *Organometallics* **1987**, *6*, 1432. The oxidation potential of (tetraphenylcyclobutadiene)cyclopentadienylcobalt is +0.90 V in dichloromethane and +1.07 V in THF vs calomel.