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Synthesis and Isolation of Polytrityl Cations by Utilizing Hexaphenylbenzene and Tetraphenylmethane Scaffolds

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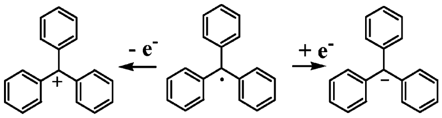
The successful isolation of stable (and soluble) hexa- and tetratrityl cations based on hexaphenylbenzene and tetraphenylmethane scaffold has been accomplished by using readily available starting materials. These robust polytrityl cations can be isolated in crystalline form and stored indefinitely at 0 °C. Their structures have been established by $^{1}H/^{13}C$ NMR spectroscopy and by UV−vis spectroscopy. The structures of these polytrityl cations were further confirmed by quantitative transformations to the reduced (poly)triphenylmethyl derivatives by hydride transfer from triethylsilane, cycloheptatriene, or a borane−dimethyl sulfide complex.

Introduction

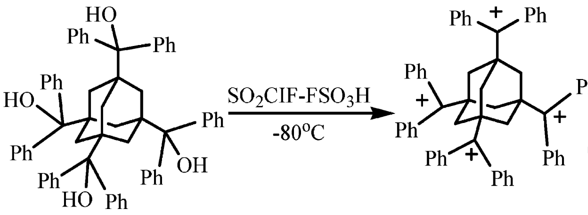
The highly stable triphenylmethyl (or trityl) cation and anion have been utilized in many facets of chemistry including in organic syntheses since the beginning of the twentieth century. The high stability of the trityl ions can be attributed to the extensive delocalization of the charge onto the phenyl rings via resonance. The trityl cation and anion are also of fundamental importance in the study of single-electron transfer (SET) mechanisms as they are formed by transfer of 1 electron to or from the triphenylmethyl radical, i.e. eq 1. All three stable derivatives of trityl (i.e. cation, anion and radical) have played important roles in organic synthesis as well as in investigation of reaction mechanisms.[1,2]



(eq. 1)

Possibly the most extensive usage of the trityl cation is found in hydride abstraction reactions both in organic syntheses and in investigation of mechanisms of organic and organometallic transformations.[3] Trityl cations have also found widespread application as one-electron oxidants,[4] and as highly effective activators for olefin polymerization reactions.[5] Recently, Marder et al.[5c] investigated how ion−ion interactions in the trityl cation and its counteranion affect the catalytic activity, stability, and, to a lesser extent, ability to stereoregulate the polymerization reactions. A variety of nonnucleophilic anions[6] have also been engineered in an important endeavor to improve catalytic activity of the trityl cation in a variety of olefin polymerization reactions.[5]

Recently, Olah et al.[7] prepared a tetrahedrally arrayed tetracation that was generated from an alcoholic precursor using magic acid (FSO_3H-SO_2ClF) and found that, unfortunately, it was stable only at low temperatures, i.e., eq 2. As such the polycationic system shown in eq 2 and its stable analogues could play a significantly important role in materials science[8] and/or in develop-



(eq. 2)

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(1) (a) Shchepinov, M. S.; Korshun, V. A. *Chem. Soc. Rev.* **2003**, *32*, 170. (b) Plack, V.; Schmutzler, R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *144−146*, 273. (c) Kobayashi, S. *Kagaku Kogyo* **1989**, *42*, 245. (d) Wu, J.-T. *Petrochemistry* **1974**, *13*, 19.

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(4) (a) Fukuzumi, S.; Ohkubo, K.; Otera, J. *J. Org. Chem.* **2001**, *66*, 1450 and references therein. (b) Hart, H.; Sulzberg, T.; Schwendeman, R. H.; Young, R. H. *Tetrahedron Lett.* **1967**, *15*, 1337. (c) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877. (d) Fukuzumi, S.; Kitano, T.; Ishikawa, M. *J. Am. Chem. Soc.* **1990**, *112*, 5631.

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(6) (a) Reed, C. A. Acc. *Chem. Res.* **1998**, *31*, 133. (b) Ivanov, S. V.; Davis, J. A.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **2003**, *42*, 4489.

(7) (a) Head, N. J.; Prakash, G. K.; Bashir-Hashemi, A.; Olah, G. A. *J. Am. Chem. Soc.* **1995**, *117*, 12005. (b) Heagy, M. D.; Wang, Q.; Olah, G. A.; Prakash, G. K. *J. Org. Chem.* **1995**, *60*, 7351.

(8) (a) MacDonald, R. A.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383. (b) Desiraju, G. R. *Crystal Engineering: The design of Organic Solids*; Elsevier: New York, 1989; p 54. (c) Zyss, J.; Josse, D.; Ledoux, I. *MCLC S&T, Sect. B*: *Nonlinear Opt.* **1994**, *7*, 169. (d) Allen, N. S. *Polym. Degrad. Stab.* **1994**, *44*, 357.

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ment of multidentate catalytic systems for the polymerization reactions.[5] Owing to the extensive utility of the trityl cation, it was conceived to design molecules containing multiple trityl sites which can serve for many of the same purposes described above, as well as the new usages (vide infra).

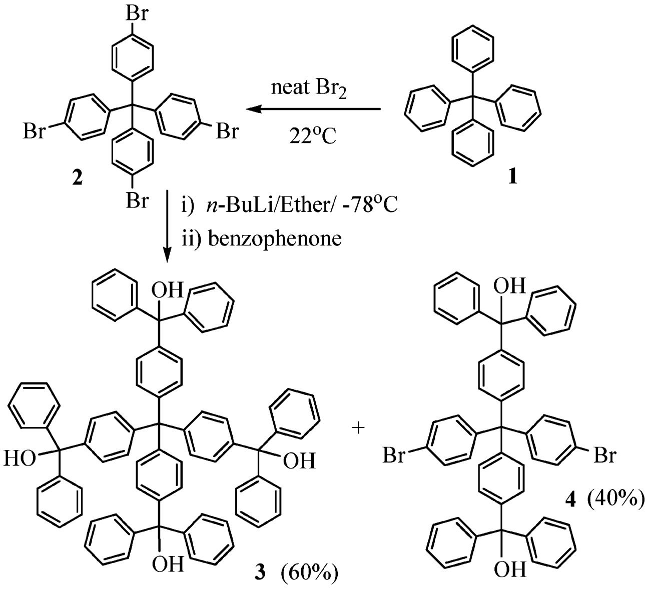
The ready availability of hexaphenylbenzene and tetraphenylmethane cores, and the ease of modification of their vertexes to incorporate suitable electroactive functionalities, makes them attractive starting points (or platforms) for the construction of nanometer-sized dendritic materials with novel light-emitting and charge-transport properties.[9,10] Accordingly, herein we now report the successful preparation of stable tetra- and hexatrityl cations by making use of tetraphenylmethane and hexaphenylbenzene platforms from readily available starting materials. The structures of these isolated (stable) polytrityl cations have been established by NMR and UV−vis spectroscopy, and further confirmed by quantitative hydride transfer reactions with cycloheptatriene, borane-dimethyl sulfide, complex, or triethylsilane (as hydride donors) to the reduced (poly)triphenylmethyl derivatives as follows.

Results and Discussion

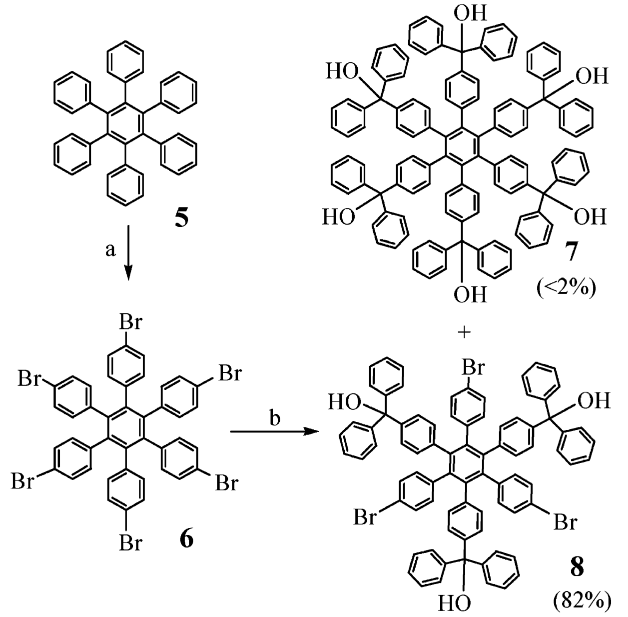
Synthesis of Alcoholic Precursors for the Polytrityl Cations Derived from Hexaphenylbenzene and Tetraphenylmethane Cores. The starting material tetrakis(4-bromophenyl)methane (**2**) for the synthesis of tetrakis(4,4-diphenyl-4-hydroxymethylphenyl)methane (**3**), the precursor to the tetratrityl cation, was available from a facile bromination of readily available tetraphenylmethane[11] (**1**) using neat bromine.[12] Lithiation of **2** with *n*-butyllithium (or *tert*-butytllithium) at −78 °C in dry diethyl ether followed by a reaction with benzophenone afforded a mixture of desired tetraalcohol **3** (∼60%) together with a product arising from an addition of benzophenone to dilithiated **2** (**4**, ∼40%), i.e., Scheme 1.

The desired symmetrical tetraalcohol **3** was easily isolated by chromatographic separation in greater than >55% yield and was characterized by $^1H/^{13}C$ NMR spectroscopy as well as by the presence of a characteristic O−H stretching in its IR spectrum, and by elemental and mass spectrometric analyses (see the Experimental Section). The ease of the synthesis of **3** from readily available tetrakis(4-bromophenyl)methane **2** prompted a similar approach for the preparation of hexaalcohol **7**, a precursor to the hexatrityl cation (see Scheme 2), from the corresponding hexakis(4-bromophenyl)benzene (**6**) as follows.

SCHEME 1



SCHEME 2[a]



[a] Reagents and conditions: (a) neat bromine, 22 °C, 96%. (b) *n*-butyllithium, −78 °C, benzophone, H_2O.

Thus, hexaphenylbenzene (**5**) treated with neat bromine at room temperature followed by trituration with cold ethanol afforded hexakis(4-bromophenyl)benzene (**6**) as a colorless solid in a nearly quantitative yield.[12] Lithiation of readily available **6** with *n*-butyllithium in diethyl ether at −78 °C followed by the reaction with benzophenone afforded a colorless solid. A chromatographic purification and structural characterization with $^1H/^{13}C$ NMR spectroscopy indicated that the symmetrical molecule obtained above was 1,3,5-tris(4-bromopheny)-2,4,6-tris(4,4-diphenyl-4-hydroxymethylphenyl)benzene (**8**) and not the expected hexaalcoholic derivative **7** (see Scheme 2).

The surprisingly selective lithiation of the alternate 4-bromophenyl groups (i.e. 1, 3, 5 positions) in **6** is

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(9) (a) Yeh, C.-H.; Lee, R.-H.; Chan, L.-H.; Lin, T.-Y.; Chen, C.-T.; Balasubramaniam, E.; Tao, Y.-T. *Chem. Mater.* **2001**, *13*, 2788. (b) Zimmermann, T. J.; Freundel, O.; Gompper, R.; Muller, J. J. J. *Eur. J. Org. Chem.* **2000**, 3305. (c) Keegstra, M. A.; Feyter, S. D.; Schryver, F. C. D.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 774. (d) Oldham, W. J., Jr.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 2987. (e) Wang, S.; Oldham, W. J., Jr.; Hudock, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *124*, 5695 and references therein. (f) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747. (g) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267 and references therein.

(10) (a) Rathore, R.; Burns, C. L.; Deselnicu, M. I. *Org. Lett.* **2001**, *3*, 2887. (b) Rathore, R.; Burns, C. L.; Abdelwahed, S. A. *Org. Lett.* submitted for publication.

(11) (a) Wassmundt, F. W.; Kiesman, W. F. *J. Org. Chem.* **1995**, *6*, 1713. (b) Zimmermann, T. J.; Muller, T. J. J. *Synthesis* **2002**, *9*, 1157.

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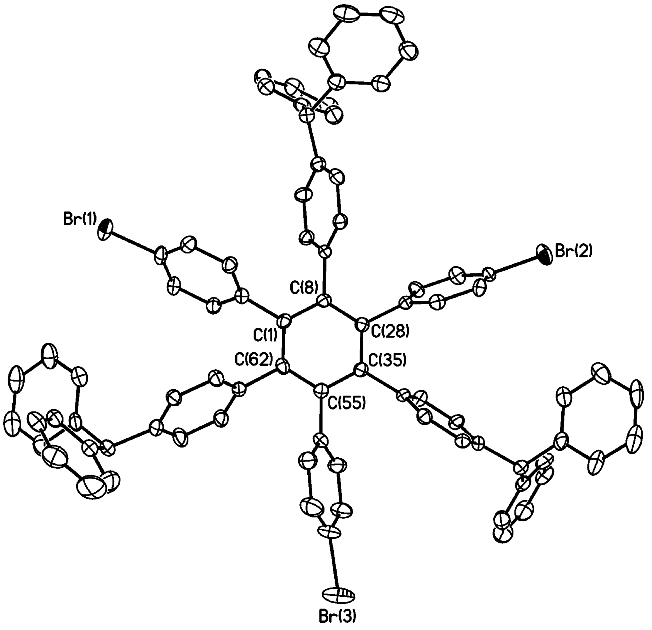
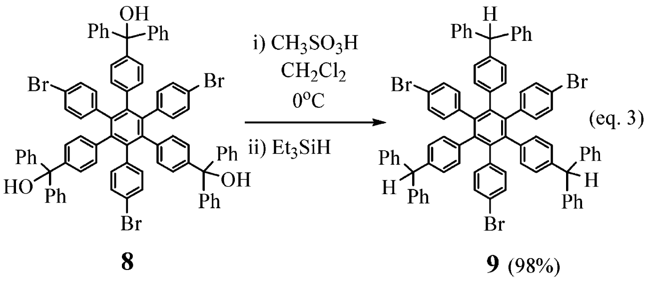


FIGURE 1. An ORTEP diagram of **9** confirming the selective lithiation/alkylation of hexakis(4-bromophenyl)benzene.

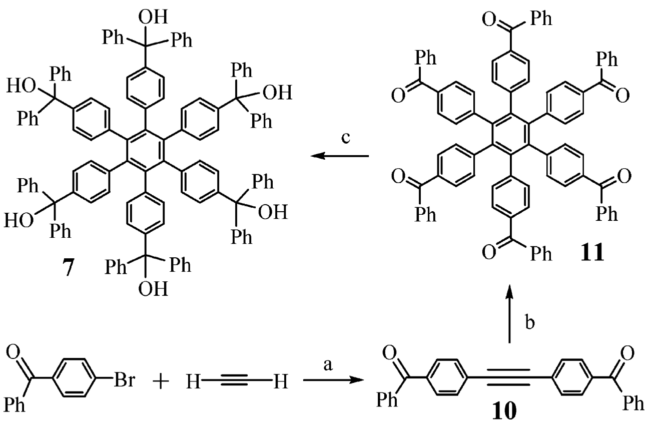
hitherto unknown, and was further confirmed by the reduction of 1,3,5-tris(4-bromophenyl)-2,4,6-tris(4,4-diphenyl-4-hydoxymethylphenyl)benzene (**8**) with triethylsilane[13] (as a hydride donor) in the presence of methanesulfonic acid in dichloromethane at 0 °C (vide infra) to **9** in excellent yield, i.e. (eq 3). The structure of the reduced **9** was established by $^1H/^{13}C$ NMR and mass spectrometry (see the Experimental Section) as well as being further confirmed by X-ray crystallography[14] (see Figure 1).



Further lithiation of **8** by with *n*-butyllithium (or *tert*-butyllithium) followed by a reaction with benzophenone yielded a complex mixture of products from which only <10% of hexaalcohol **7** (~90% pure as judged by ^1H NMR spectroscopy) could be isolated by tedious chromatographic separation. Clearly, a new approach was necessary for a successful preparation of the desired hexatrityl precursor **7**.

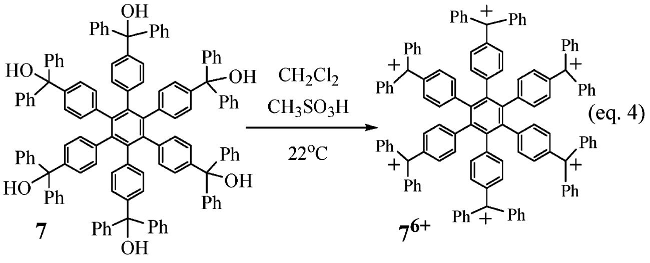
It was conceived that an addition of excess phenyllithium to hexakis(4-benzoylphenyl)benzene **11** (see Scheme 3) may allow direct access to **7**. Thus, bis(4-benzoylphenyl)acetylene (**10**), easily obtained by a Pd-catalyzed coupling of commercially available 4-bromobenzophenone with gaseous acetylene in 65% yield, was trimerized in refluxing dioxane in the presence of dicobaltoctacarbonyl as a catalyst to the previously unknown hexakis(4-benzoylphenyl)benzene (**11**). A reaction of excess phenyllithium with **11** afforded the hexaalcohol **7** in almost quantitative yield. The simplicity of ^1H and ^{13}C NMR spectra together with a characteristic O−H stretching frequency at 3554 cm^{-1} (and the lack of absorptions due to the carbonyl groups) in the IR spectrum readily confirmed the structure of desired hexaalcohol **7** (see the Experimental Section).

SCHEME 3[a]



[a] Reagents and conditions: (a) $(PPh_3)_2PdCl_2$, CuI, CH_3CN/piperdine, reflux; (b) $Co_2(CO)_8$, dioxane, reflux; (c) phenyl lithium, 0 °C, H_2O.

Generation and Spectroscopic Analysis of Hexa- and Tetratrityl Cations from Alcoholic Precursors 3 and 7 in Solution. The polytrityl cations from alcoholic precursors **3** and **7** were readily generated in solution by reaction with a strong acid, such as trifluoroacetic acid, methanesulfonic acid, or tetrafluoroboric acid, in dichloromethane at 22 °C, e.g. eq 4. The highly colored (and soluble) tetra- and hexatrityl cations ($\mathbf{3}^{4+}$ and $\mathbf{7}^{6+}$) were (UV−vis) spectroscopically identical irrespective of the acid used (vide infra). Moreover, the dark-colored solutions of the polytrityl cations $\mathbf{3}^{4+}$ and $\mathbf{7}^{6+}$ were found to be stable for prolonged periods at room temperature. The robustness of these polytrityl cations allowed their structures to be established by ^1H and ^{13}C NMR spectroscopy at ambient temperatures as follows.



NMR Spectroscopy. Thus, Figure 2 shows the ^1H NMR spectra of tetratrityl cation $\mathbf{3}^{4+}$, hexatrityl cation $\mathbf{7}^{6+}$, and for the sake of comparison, the spectrum of the triphenylmethyl cation ($\mathbf{12}^{+}$) together with their alcoholic precursors **3**, **7**, and triphenylmethanol (**12**). The chemical shifts of various protons in trityl cations as well as of their alcoholic precursors are also listed in Table 1. The

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[13] (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. (b) Also see: Badejo, I. T.; Karaman, R.; Fry, J. L. *J. Org. Chem.* **1989**, *54*, 4591.

[14] A precise structure of **9** could not be determined due to the disordered solvent molecules.

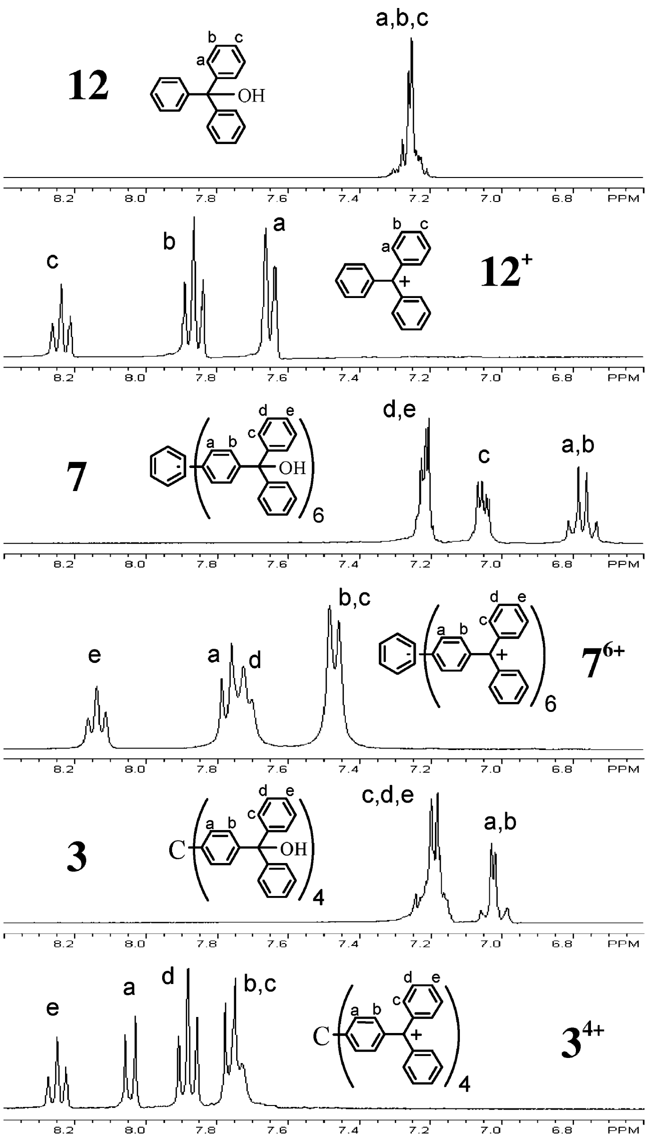

FIGURE 2. ^{1}H NMR spectra of various trityl tetrafluoroborate salts and their alcoholic precursors in CD_2Cl_2 at 22 °C.

TABLE 1. Comparison of the ^{1}H NMR Chemical Shifts (ppm) of Various Trityl Cations and Their Alcoholic Precursors in CD_2Cl_2

	alcoholic precursor		tritiyl cation[a]
12	7.20−7.31 (m, 15H) 2.80 (s, 1H, −OH)	$\mathbf{12}^+$	7.67 (d, J = 7.6 Hz, 6H) 7.88 (t, J = 7.6 Hz, 6H) 8.26 (t, J = 7.7 Hz, 3H)
3	7.03 (sym m, 16H) 7.14−7.24 (m, 40H) 2.75 (s, 4H, −OH)	$\mathbf{3}^{4+}$	7.66−7.79 (m, 24H) 7.88 (d, J = 8.4 Hz, 16H) 8.04 (d, J = 8.4 Hz, 8H) 8.25 (t, J = 7.2 Hz, 8H)
7	6.78 (sym m, 24H) 7.02−7.09 (m, 24H) 7.20−7.25 (m, 36H) 2.82 (s, 6H, −OH)	$\mathbf{7}^{6+}$	7.47 (br d, J = 8.0 Hz, 36H) 7.71 (t, J = 7.4 Hz, 24H) 7.76 (d, J = 8.2 Hz, 12H) 8.14 (t, J = 7.4 Hz, 12H)

[a] The cations were generated causing excess $HBF_4{\cdot}OEt_2$.

simplicity and similarity of the proton spectra of the tetra- and hexatrityl cations to that of the parent trityl cation $\mathbf{12}^+$ confirmed the formation of highly symmetrical $\mathbf{3}^{4+}$ and $\mathbf{7}^{6+}$. The proton NMR chemical shifts for the parent trityl cation have been assigned as follows, $\delta = 8.26$ (triplet, the para ring protons), $\delta = 7.88$ (triplet, the meta ring protons), and $\delta = 7.67$ (doublet, the ortho ring protons) ppm, and were consistent with the earlier assignment of Farnum.[15] In a similar vein, the ^{1}H NMR chemical shifts for the hexatrityl $\mathbf{7}^{6+}$ and tetratrityl $\mathbf{3}^{4+}$ cations can be assigned as indicated in Figure 2 and compiled in Table 1. A further structural confirmation of these symmetrical polytrityl cations ($\mathbf{3}^{4+}$ and $\mathbf{7}^{6+}$) was obtained by observation of a single distinctive peak, for the positively charged carbon, in their ^{13}C NMR spectra at 209.73 ppm, triphenylmethyl cation $\mathbf{12}^+$; 208.15 ppm, $\mathbf{3}^{4+}$; and 208.22 ppm, $\mathbf{7}^{6+}$.

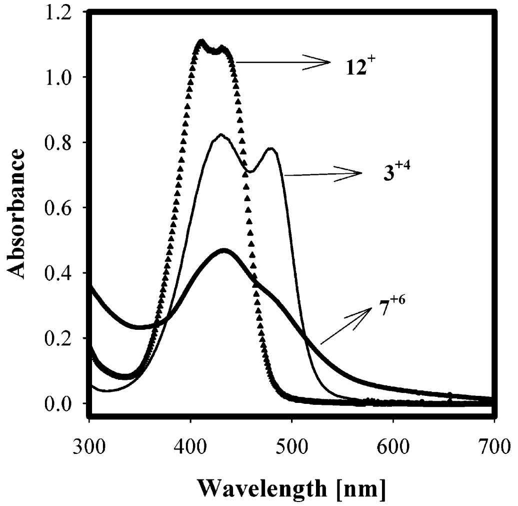

FIGURE 3. The UV−vis absorption spectra of various trityl cations in dichloromethane at 22 °C.

UV−Vis Spectral Analysis of Hexa- and Tetratrityl Cations $\mathbf{3}^{4+}$ and $\mathbf{7}^{6+}$. The UV−vis absorption spectra of the various cations prepared as above are shown in Figure 3. The parent trityl cation showed a twin absorption band at $\lambda_{max} = 410$ and 432 nm and was the same as reported previously.[16] The UV−vis absorption spectra of tetracation $\mathbf{3}^{4+}$ ($\lambda_{max} = 430$ and 474 nm) and hexacation $\mathbf{7}^{6+}$ ($\lambda_{max} = 434$ and 481 nm) showed red-shifted (twin) absorption bands as compared to the parent trityl cation (see Figure 3). The extensive distortion and the red shift in the absorption bands of the hexacation $\mathbf{7}^{6+}$ may be attributed to the electronic interactions between various trityl groups via the propeller of the hexaphenyl ring system.[10b] Note that one of the phenyl rings of each trityl unit is also part of the propeller of the hexaphenylbenzene core.

Quantitative UV−vis spectroscopic analysis of the highly colored solutions of $\mathbf{3}^{4+}$, $\mathbf{7}^{6+}$, and $\mathbf{12}^+$ allowed the determination of the molar extinction coefficients of the multiply charged cations in comparison to the parent trityl cation $\mathbf{12}^+$ and the values are listed in Table 2. The measured extinction coefficient of 35 ,300 ± 200 M^{-1} cm^{-1} for the triphenylmethyl cation ($\mathbf{12}^+$) was found to be in good agreement with that of the reported value.[16] Interestingly, a comparison of the extinction coefficient of the monocation ($\mathbf{12}^+$) with that of the hexacation $\mathbf{7}^{6+}$ showed

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[15] (a) Farnum, D. G. *J. Am. Chem. Soc.* **1964**, *86*, 934. (b) Also see: Farnum, D. G. *Adv. Phys. Org. Chem.* **1975**, *11*, 123.

[16] Shida, T. *Electronic Absorption Spectra of radical Ions*; Elsevier: Amsterdam, The Netherlands, 1988.

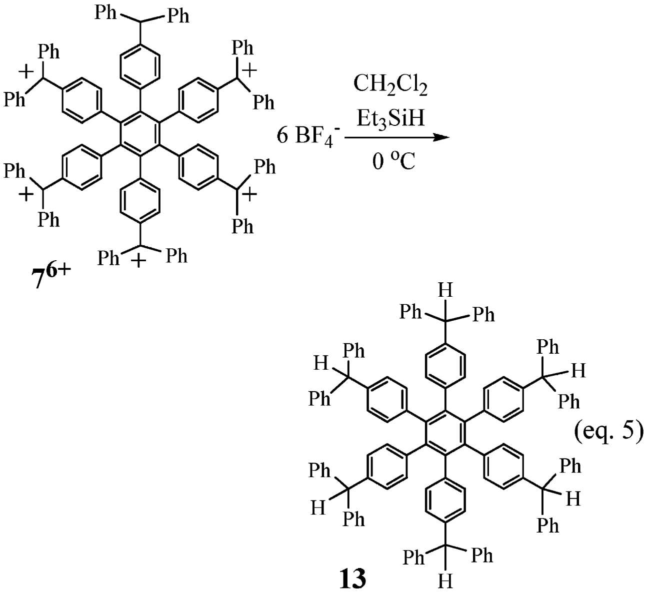
TABLE 2. UV–Vis Absorption Data for Various Trityl Cations in CH_2Cl_2 Generated from the Corresponding Alcoholic Precursors with HBF_4 at 22 °C

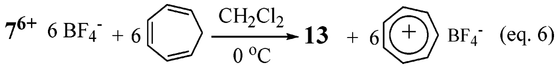
trityl cation[a]	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})
$\mathbf{12}^{+}$	410, 432	35 300 ± 300
$\mathbf{3}^{4+}$	430, 474	133 000 ± 500
$\mathbf{7}^{6+}$	434, 481	177 600 ± 500

the latter to be approximately six times the value of the model compound. Moreover, the value of the extinction coefficient for the tetracation $\mathbf{3}^{4+}$ was roughly four times that of the parent trityl cation. As such, the comparison of the molar extinction coefficients of polytrityl cations $\mathbf{3}^{4+}$ and $\mathbf{7}^{6+}$ to that of the model trityl cation ($\mathbf{12}^{+}$) further supports the structural identity of these polycations arrived at by NMR spectroscopy.

Encouraged by the stability of these polytrityl cations in solution, attempts were made for their isolation in the solid state as follows. Thus, a solution of tetraalcohol **3** in dichloromethane was treated with a 20% excess tetrafluoroboric acid/diethyl ether complex at 0 °C. The resulting dark red solution was layered with dry hexanes and was stored in a refrigerator (−25 °C) for 24 h. The dark-colored microcrystalline precipitate of the tetracation [$\mathbf{3}^{4+}$ $(BF_4^-)_4$] thus obtained was filtered (using a cintered glass funnel) and washed with dry hexanes and dried in vacuo (yield: 73%). The UV−vis absorption spectrum as well as the ^1H NMR spectrum of the resulting crystalline tetracation in CD_2Cl_2 were identical with those obtained above (see Figures 2 and 3). Similarly, the hexatrityl cation [$\mathbf{7}^{6+}$ $(BF_4^-)_6$] can be isolated in 78% yield; and both of these polytrityl cations were stable for prolonged periods if stored at 0 °C. However, repeated attempts to obtain single crystals suitable for X-ray crystallography of [$\mathbf{3}^{4+}$ $(BF_4^-)_4$] and [$\mathbf{7}^{6+}$ $(BF_4^-)_6$] were thus far unsuccessful.

Chemical Reactivity of Hexa- and Tetratrityl Cations $\mathbf{3}^{4+}$ and $\mathbf{7}^{6+}$. An independent confirmation of the structures of the crystalline polytrityl cations was also obtained by their clean and quantitative reduction to the (poly)triphenylmethyl derivatives (see the Experimental Section) by using triethylsilane, borane−dimethyl sulfide complex, or cycloheptatriene as a hydride donor. For example, treatment of a dark-red solution of microcrystalline hexatrityl cation [$\mathbf{7}^{6+}$ $(BF_4^-)_6$] (prepared as above)-in dichloromethane at 0 °C with 6 equiv of triethylsilane resulted in the immediate decolorization of the orange-red solution. A standard aqueous workup of the resulting solution afforded a white solid that was characterized by various spectroscopic methods and by elemental analysis (see the Experimental Section), and was shown to be hexakis(4-diphenylmethylphenyl)benzene **13**, i.e. eq 5. A similar treatment of $\mathbf{7}^{6+}$ and $\mathbf{3}^{4+}$ with borane−dimethyl sulfide complex or triethylsilane in dichloromethane afforded the corresponding reduced (poly)diphenylmethyl derivatives (**13** and **14**, respectively) in quantitative yields. Moreover, reaction of a dichloromethane solution of $\mathbf{7}^{6+}$ with cycloheptatriene afforded a colorless solution within 10 min. Addition of hexanes precipitated tropylium tetrafluoroborate salt, which was filtered, and the filtrate was shown to contain the reduced **13** in almost quantitative yield, i.e., eq 6. The identity of the tropylium salt[17] was confirmed by comparison of the $^1H/^{13}C$ NMR spectra with that of an authentic sample.





Summary. In summary, a successful synthesis and isolation of hexa- and tetratrityl cations has been accomplished by using readily available starting materials, and their structures have been established by $^1H/^{13}C$ NMR and UV−vis spectroscopy as well as by quantitative hydride transfer from borane−dimethyl sulfide complex, triethylsilane, or cycloheptatriene. We are now actively exploring the cocrystallization of these polytrityl cations with a variety of nonnucleophilic anions[6] for usage as catalysts for polymerization reactions as well as with redox-active spherical polyoxometalate (poly)anions[18] to exploit their material properties. These polytrityl cations also hold potential for the preparation of polytrityl radicals, which may possess interesting magnetic properties.[19]

Experimental Section

Tetrakis(4-bromophenyl)methane (2). A 500-mL, two-necked flask equipped with a magnetic stirring bar and an outlet adapter connected via rubber tubing to a pipet that is immersed in an aqueous sodium hydroxide solution (10%, 250 mL) is charged with 18 g (50 mmol) of powdered tetraphenylmethane (**1**). Neat bromine (0.35 mol, 20 mL) is added slowly during a 5-min period while the reaction mixture is stirred. The reaction starts immediately as judged by an evolution of gaseous hydrobromic acid. After the addition of bromine, the dark-orange slurry is stirred for an additional 20 min and the resulting slurry is poured into ethanol (250 mL) cooled in a dry ice−acetone bath. The precipitated solid was filtered and washed with an aqueous sodium bisulfite solution. The crude material was recrystallized from chloroform/ethanol to afford pure **2** as a crystalline solid in nearly quantitative yield (34.8 g, 97%); mp 312.5−313 °C (lit.[20] mp 312−313 °C); ^1H NMR

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(CDCl$_3$) δ 7.01 (d, J = 6 Hz, 8 H), 7.39 (d, J = 6 Hz, 8 H); ^{13}C NMR (CDCl$_3$) δ 65.9, 120.6, 130.8, 132.1, 144.0.

Tetrakis(4-diphenyl-4-hydroxymethylphenyl)methane (3). To a cooled (−78 °C) solution of tetrakis(4-bromophenyl)methane (**2**; 2.20 g, 3.46 mmol) in anhydrous diethyl ether (35 mL) was added dropwise *n*-butyllithium (2.5 M in hexane, 6.92 mL, 17.3 mmol) under an argon atmosphere. The resulting reaction mixture was allowed to warm to −30 °C over a 1-h period, and then stirred at −30 °C for an additional 1 h before adding solid benzophenone (3.15 g, 17.3 mmol). The reaction mixture was stirred for 12 h and quenched by water. The organic products were extracted with CH$_2$Cl$_2$ (3 × 50 mL) and dried over anhydrous magnesium sulfate. The crude product was purified by flash chromatography with a 10% ethyl acetate/90% hexanes mixture to afford **3** and **4** as colorless solids. The spectral data are given as follows. Tetrakis(4-diphenyl-4-hydroxymethylphenyl)methane (**3**): yield 58%; mp 220 °C (acetone); ^{1}H NMR (CDCl$_3$) δ 2.75 (s, 4H), 7.03 (sym m, 16H), 7.14−7.24 (m, 40H); ^{13}C NMR (CDCl$_3$) δ 64.2, 82.0, 127.0, 127.5, 127.7, 130.3, 132.5, 144.3, 144.6, 146.2; IR (KBR) 3456.7 (m), 3055.9 (m), 3026.5 (m), 1490.0 (s), 1446.2 (s), 1010.1 (s), 821.1 (m), 759.7 (s), 699.1 (s) cm^{-1}; FAB *m/z* 1049 (M$^+$), 1049 calcd for $C_{77}H_{60}O_4$. Anal. Calcd for $C_{77}H_{60}O_4$: C, 88.14; H, 5.76; O, 6.10. Found: C, 88.32; H, 5.46. Bis(4-bromophenyl)bis(4,4-diphenyl-4-hydroxymethyl-phenyl)methane (**4**): yield 36%; mp 290 °C (dichloromethane-hexanes); ^{1}H NMR (CDCl$_3$) δ 2.79 (s, 2H), 7.00−7.12 (m, 16H), 71.9−7.33 (m, 40H); ^{13}C NMR (CDCl$_3$) δ 64.1, 82.0, 126.91, 127.0, 127.5, 127.7, 130.3, 132.5, 144.2, 144.5, 146.2; IR (KBr) 3457.2 (m), 3055.8 (m), 3027.4 (m), 1490.2 (s), 1446.0 (s), 1010.6 (s), 821.3 (m), 760.0 (s), 699.4 (s) cm^{-1}; FAB *m/z* 842 (M$^+$), 842 calcd for $C_{51}H_{38}O_2Br_2$. Anal. Calcd for $C_{51}H_{38}O_2Br_2$: C, 72.69; H, 4.55; Br, 18.96; O, 3.80. Found: C, 72.48; H, 4.36.

Hexakis(4-bromophenyl)benzene (6). A 500-mL, two-necked flask equipped with a magnetic stirring bar and an outlet adapter connected via rubber tubing to a pipet that is immersed in an aqueous sodium hydroxide solution (10%, 250 mL) is charged with 26.7 g (50 mmol) of powdered hexaphenylbenzene (**5**). Neat bromine (0.69 mol, 40 mL) is added slowly during a 5-min period while the reaction mixture is stirred. The reaction starts immediately as judged by an evolution of gaseous hydrobromic acid. After the addition of bromine, the dark-orange slurry is stirred for an additional 45 min and the resulting slurry is poured into ethanol (500 mL) cooled in a dry ice−acetone bath. The precipitated product was filtered and washed with an aqueous sodium bisulfite solution. The crude material was recrystallized from tetrahydrofuran/hexanes to afford pure **6** as a colorless solid in nearly quantitative yield (96%): mp 355−357 °C; ^{1}H NMR (CDCl$_3$) δ 6.61 (d, J = 8.1 Hz, 12H), 7.07 (d, J = 8.1 Hz, 12H); ^{13}C NMR (CDCl$_3$) δ 120.1, 130.2, 132.2, 138.0, 139.2; FAB *m/z* 1008 (M$^+$), 1008 calcd for $C_{42}H_{24}Br_6$. Anal. Calcd for $C_{42}H_{24}Br_6$: C, 50.04; H, 2.40; Br, 47.56. Found: C, 50.25; H, 2.37.

1,3,5-Tris(4-bromophenyl)-2,4,6-tris(4-diphenyl-4-hydroxymethyl-phenyl)benzene (8). Anhydrous THF (40 mL) was added to hexakis(4-bromophenyl)benzene (2.02 g, 2.00 mmol) under an argon atmosphere. The solution was brought to −78 °C and *tert*-butyllithium (1.7 M solution in pentane, 8.8 mL, 14.4 mmol) was added dropwise. The reaction mixture was allowed to slowly warm to −10 °C over 40 min and stirred at this temperature for 30 min before adding benzophenone (3.63 g, 15.0 mmol). The reaction was allowed to warm to 22 °C and was stirred for 2 h. The product was extracted with CH$_2$Cl$_2$ (3 × 50 mL) and the organic extracts were dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the product was purified by flash chromatography on silica gel with ethyl acetate/hexanes mixture as eluent to afford **8** as a colorless solid. Yield 82; mp 281 °C (hexanes−dichloromethane); ^{1}H NMR (CDCl$_3$) δ 2.77 (s, 3 H), 6.63−6.83 (m, 24 H) 6.96−7.05 (m, 12 H), 7.22−7.30 (m, 18 H); ^{13}C NMR (CDCl$_3$) δ 81.7, 119.7, 126.8, 127.2, 127.86, 127.89, 130.0, 130.6, 132.9, 138.9, 139.1, 139.4, 140.2, 144.2, 146.7; IR (KBr) 3543.5 (m), 3465.6 (m), 3057.2 (m), 3028.2 (m), 1488.0 (s), 1446.2 (s), 1010.9 (s), 830.4 (m), 755.2 (s), 699.2 (s) cm^{-1}; FAB *m/z* 1318 (M$^+$), 1318 calcd for $C_{81}H_{57}Br_3O_3$. Anal. Calcd for $C_{81}H_{57}Br_3O_3$: C, 73.81; H, 4.36; Br, 18.19; O, 3.64. Found: C, 73.96; H, 4.26.

1,3,5-Tris(4-bromophenyl)-2,4,6-tris(4-diphenyl-4-methylphenyl)benzene (9). To a cooled (~0 °C) solution of 1,3,5-tris(4-bromophenyl)-2,4,6-tris(4-diphenyl-4-hydroxymethylphenyl)benzene (0.244 g, 0.186 mmol) in anhydrous dichloromethane (20 mL) was added a diethyl ether solution of tetrafluoroboric acid (0.13 mL, 1.8 mmol) under an argon atmosphere. The resulting dark-red solution (UV−vis, λ_{max} = 418 and 513 nm; ϵ_{418} = 99 000 ± 1 000 M^{-1} cm^{-1}) was stirred for 10 min before the addition of the borane−dimethyl sulfide complex (1 M in CH$_2$Cl$_2$, 1 mL, 1 mmol). After being stirred for 10 min, the colorless reaction mixture was quenched with saturated aqueous sodium bicarbonate solution (20 mL) and diluted with dichloromethane (50 mL). The organic layer was separated and washed with water (3 × 25 mL) and dried over anhydrous magnesium sulfate and evaporated. The resulting solid was crystallized from a dichloromethane/hexanes mixture. Yield 74%; mp 280−281 °C; ^{1}H NMR (CDCl$_3$) δ 5.44 (s, 3 H), 6.67−6.79 (m, 18 H), 6.88−7.00 (m, 12 H), 7.09−7.11 (m, 6 H), 7.20−7.28 (m, 6 H), 7.31−7.36 (m, 12 H); ^{13}C NMR (CDCl$_3$) δ 56.2, 120.0, 126.6, 128.7, 130.0, 130.4, 131.5, 133.3, 138.3, 139.9, 140.8, 141.8, 144.4; FAB *m/z* 1270 (M$^+$), 1270 calcd for $C_{81}H_{57}Br_3$. Anal. Calcd for $C_{81}H_{57}Br_3$: C, 76.60; H, 4.52; Br, 18.87. Found: C, 76.51 H, 4.48.

Bis(4-benzoylphenyl)acetylene (10). Triphenylphosphine (3.15 g, 12 mmol), 4-bromobenzophenone (19.60 g, 75 mmol), piperidine (30 mL, 305 mmol), and acetonitrile (30 mL, 580 mmol) were placed in a three-necked, round-bottomed flask that was repeatedly evacuated and filled with argon. Copper iodide (0.5 g, 2.6 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.53 g, 0.75 mmol) were added to the reaction mixture and pure acetylene gas was bubbled into the yellow mixture for 6 h while refluxing. The reaction mixture was further refluxed for 12 h, cooled to 22 °C, and evaporated in vacuo. The dark crude solid was triturated with dichloromethane (5 × 50 mL) and the desired product precipitated in the organic layer upon standing. The microcrystalline precipitate of **10** was filtered and recrystallized further from a dichloromethane/hexanes mixture. Yield 85%; mp 228−230 °C (hexanes−dichloromethane); ^{1}H NMR (CDCl$_3$) δ 7.51 (sym m, 4H), 7.61 (sym m, 2H), 7.67 (sym m, 4H), 7.79−7.83 (m, 8H); ^{13}C NMR (CDCl$_3$) δ 91.6, 126.6, 128.1, 129.7, 129.8, 131.9, 132.4, 136.8, 136.9, 195.0; IR (KBr) 2240.2 (w), 1646.8 (s), 1603.7 (m), 1444.6 (m), 1288.1 (m), 1144.6 (w), 922.1 (w), 789.6 (w), 739.6 (m), 691.4 (s), 680.7 (m) cm^{-1}; GCMS *m/z* 386 (M$^+$), 386 calcd for $C_{28}H_{18}O_2$. Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69; O, 8.28. Found: C, 86.89; H, 4.53.

Hexakis(4-benzoylphenyl)benzene (11). Octacarbonyldicobalt (50 mg, 0.147 mmol) and bis(4-benzoylphenyl)acetylene (4.0 g, 10.3 mmol) were placed in a 100-mL Schlenk flask under an argon atmosphere. After addition of 1,4-dioxane (120 mL), the reaction was refluxed for 12 h. The solvent was removed in vacuo and the resulting crude solid was chromatographed on a short silica gel pad. Initial elution with dichloromethane afforded the unreacted bis(4-benzoylphenyl)acetylene (0.96 g, 24%) followed by elution with a mixture of dichloromethane (containing 1% methanol) to furnish the desired hexakis(4-benzoylphenyl)benzene **11** (2.9 g, 73%). The hexakis(4-benzoylphenyl)benzene was further recrystallized from a dichloromethane/hexanes mixture to afford a pale yellow crystalline solid: yield 95% based on the reacted bis(4-benzoylphenyl)acetylene.

Alternatively, bis(benzonitrile)palladium(II) dichloride (0.250 g, 0.73 mmol) was added to a Schlenk flask (under argon atmosphere) containing bis(4-benzoylphenyl)acetylene (1.0 g,

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2.6 mmol) and benzene (100 mL). The reaction was allowed to reflux for 12 h before the solvent was removed and the product was redissolved in dichloromethane. It was then run through a silica gel pad and the silica gel pad was washed with CH_2Cl_2, which allowed the recovery of the starting bis-(4-benzoylphenyl)acetylene (45%). A further elution of the silica gel column with a mixture of dichloromethane/methanol (~1%) afforded the desired hexakis(4-benzoylphenyl)benzene (53%): mp 278−280 °C (hexanes−dichloromethane); ^{1}H NMR ($CDCl_3$) δ 7.02−7.08 (sym m, 12H), 7.36−7.46 (m, 24H), 7.49−7.54 (m, 6H), 7.55−7.61 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 128.0, 128.8, 129.5, 130.7, 132.1, 134.9, 137.0, 139.5, 143.3, 195.2; IR (KBr) 3293.3 (w), 3047.5 (w), 1652.7 (s), 1604.4 (s), 1445.6 (m), 1307.8 (s), 1277.6 (s), 940.5 (m), 731.9 (s), 701.5 (s) cm^{-1}; FAB *m/z* 1159 (M$^+$), 1159 calcd for $C_{84}H_{54}O_6$. Anal. Calcd for $C_{84}H_{54}O_6$: C, 87.02; H, 4.69; O, 8.28. Found: C, 86.92; H, 4.59.

Hexakis(4-diphenyl-4-hydroxymethylphenyl)benzene (7). Hexakis(4-benzoylphenyl)benzene (0.50 g, 0.43 mmol) and dry ether (50 mL) were placed in a Schlenk flask under an argon atmosphere. The reaction flask was cooled to −40 °C and a cyclohexanes−ether solution of phenyllithium (3 mmol) was added. The reaction was allowed to warm to 22 °C while stirring was continued for 5 h and was quenched with water. The reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL) and dried over anhydrous magnesium sulfate. The crude material was purified by flash chromatography on silica gel, using an ethyl acetate/hexane mixture as eluent to afford **7** as a white solid. Yield 88%; mp 260 °C (acetone); ^{1}H NMR ($CDCl_3$) δ 2.82 (s, 6H), 6.78 (d, J = 8.7 Hz, 24H), 7.02−7.09 (m, 24H), 7.20−7.25 (m, 36H); ^{13}C NMR ($CDCl_3$) δ 81.9, 126.1, 126.9, 127.5, 127.6, 130.8, 139.2, 139.7, 143.7, 146.4; IR (KBr) 3554.2 (m), 3452.3 (m), 3055.0 (m), 3025.9 (m), 1490.2 (m), 1445.8 (m), 1012.3 (m), 756.0 (s), 699.6 (s) cm^{-1}; FAB *m/z* 1628 (M$^+$), 1628 calcd for $C_{120}H_{90}O_6$. Anal. Calcd for $C_{120}H_{90}O_6$: C, 88.53; H, 5.57; O, 5.90. Found: C, 88.23; H, 5.48.

General Procedure for the Isolation of Crystalline Trityl Cations. The alcoholic precursor (0.2 mmol) was dissolved in dichloromethane (15 mL) and was treated with an excess solution of tetrafluoroboric acid/diethyl ether complex at ~0 °C under an argon atmosphere. The resulting dark-colored solution was carefully layered with dry hexanes (30 mL) and placed in a refrigerator (−25 °C). During the course of 1 to 3 days, dark microcrystalline salt was deposited that was filtered cold with use of a cintered glass funnel, washed with hexanes, and dried in vacuo. The yields and spectral data for various trityl cations prepared according to this procedure are summarized below.

Triphenylmethyl or trityl cation (12^+): yield 42%; ^{1}H NMR (CD_2Cl_2) δ 7.67 (d, J = 7.6 Hz, 6H), 7.88 (t, J = 7.6 Hz, 6H), 8.26 (t, J = 7.7 Hz, 3H); ^{13}C NMR (CD_2Cl_2) δ 130.2, 139.4, 142.2, 143.0, 209.7. **Tetratrityl cation (3^{4+}):** yield 73%; ^{1}H NMR (CD_2Cl_2) δ 7.66−7.79 (m, 24H), 7.88 (d, J = 8.4 Hz, 16H), 8.04 (d, J = 8.4 Hz, 8H), 8.25 (t, J = 7.2 Hz, 8H); ^{13}C NMR (CD_2Cl_2) δ 62.2, 130.1, 131.8, 138.3, 142.3, 142.6, 142.9, 208.2. **Hexatrityl cation (7^{6+}):** yield 78%; ^{1}H NMR (CD_2Cl_2) δ 7.47 (br d, J = 8.0 Hz, 36H), 7.71 (t, J = 7.4 Hz, 24H), 7.76 (d, J = 8.2 Hz, 12H), 8.14 (t, J = 7.4 Hz, 12H); ^{13}C NMR (CD_2Cl_2) δ 137.8, 138.98, 139.14, 139.25, 141.60, 141.81, 142.01, 142.50, 142.67, 153.1, 208.2. [Also note that the reduction of various polytrityl cations can also be performed with various hydride donors without isolation of the cation according to the procedure detailed for the reduction of trialcohol **8** to the corresponding triphenylmethyl derivative **9** above.]

General Procedure for the Reaction of Crystalline Trityl Cations with Various Hydride Donors. To a solution of isolated polytrityl cation (0.05 mmol) in anhydrous dichloromethane (10 mL) at 0 °C was added 10−20% excess of a hydride donor (such as borane−dimethyl sulfide complex, triethylsilane, or cycloheptatriene) under an argon atmosphere. The resulting mixture was stirred for 10 min, quenched with saturated aqueous sodium bicarbonate solution (20 mL), and then diluted with dichloromethane (20 mL). The organic layer was washed with water (3 × 25 mL) and dried over anhydrous magnesium sulfate and evaporated to afford the corresponding triphenylmethyl derivative as a colorless solid. The spectral data for various triphenylmethyl derivatives **13** and **14** are summarized below.

Hexakis(4-diphenyl-4-methylphenyl)benzene (13): mp 235−237 °C; ^{1}H NMR ($CDCl_3$) δ 5.39 (s, 6H), 6.63 (d, J = 8.4 Hz, 12H), 6.71 (d, J = 8.1 Hz, 12H), 6.90−6.96 (m, 24H), 7.17−7.25 (m, 36H); ^{13}C NMR ($CDCl_3$) δ 56.6, 125.8, 127.4, 127.9, 129.1, 131.3, 138.4, 139.7, 140.1, 143.6; FAB *m/z* 1532 (M$^+$), 1532 calcd for $C_{120}H_{90}$. Anal. Calcd for $C_{120}H_{90}$: C, 94.08; H, 5.92. Found: C, 94.00; H, 5.86.

Tetrakis(4-diphenyl-4-methylphenyl)methane (14): ^{1}H NMR ($CDCl_3$) δ 5.47 (s, 4 H), 6.89−7.31 (m, 56 H); ^{13}C NMR ($CDCl_3$)δ 56.8, 64.1, 126.0, 128.0, 128.2, 129.1, 130.6, 141.2, 143.4, 143.7; FAB *m/z* 984 (M$^+$), 984 calcd for $C_{77}H_{60}$. Anal. Calcd for $C_{77}H_{60}$: C, 93.86; H, 6.14. Found: C, 93.69; H, 6.10.

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Supporting Information Available: Tables of X-ray crystallographic data for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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