An Approach Towards Functional Dendrimers Based on the Hydroboration Reaction and Spontaneous Boron–Nitrogen Bond Formation

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Keywords: Boranes / Dendrimers / Hydroboration / N ligands

The reaction of 1,4-bis- or 1,3,5-tris(bromoboryl)benzenes **4** and **6**, respectively, with 2 or 3 equiv. of 4,4′-bis(but-3′′-enyl)-2,2′-bipyridyl (**2**) leads to the corresponding 2,2′-bipyridylboronium cations **5** and **7** in almost quantitative yield. Using the monocation $[(MeC_6H_4)B(Br)\{4,4'$-bis(but-3′′-enyl)-2,2′-bipyridyl$\}]^+$ (**3Br**) as a model system, it is shown that the olefinic side-chains of such compounds are readily transformed into alkyldibromoborane functionalities by hydroboration with $HBBr_2$. Subsequent addition of 4,4′-dimethyl-2,2′-bipyridyl leads to the formation of a branched system of three 2,2′-bipyridylboronium cations (**9Br**). The species **5** and **7** can be regarded as generation zero (G_0) 2,2′-bipyridylboronium dendrimers, and the hydroboration/B–N adduct formation sequence offers a convenient route for the assembly of higher generations.

Introduction

Dendrimers are macromolecules with well-defined molecular architectures derived from a central atom or core with multiple branches. They are gaining great attention due to their potential applications in, for example, biology, catalysis and materials science. Apart from purely organic dendrimers, metallodendrimers[1–3] and heteroatom-based dendrimers[4–6] represent an important area of research. In 1994, Puddephatt reported organometallic dendrimers featuring (2,2′-bipyridyl)Pt^{IV} chelates in every generation.[7,8] Since then, numerous dendrimers incorporating (polypyridyl)metal complexes have been synthesised, mainly with the aim of studying photoinduced energy transfer and multielectron redox processes.[9]

Research in our group focuses on the chemistry of main group chelates of the 2,2′-bipyridyl (bipy) ligand, particularly on 2,2′-bipyridylboronium cations **A** (Figure 1), which are relatives of the organic electron acceptor Diquat (**B**; Figure 1) and thus behave as reversible two-electron redox systems.[10–15]

Cations **A** form spontaneously and under very mild conditions upon treatment of haloboranes XBR_2 (X = Cl, Br) with 2,2′-bipyridyl. For example, starting from 1,1′,3,3′-tetrakis(bromoboryl)ferrocene, the ferrocene derivative **C** (Figure 1) bearing four redox-active 2,2′-bipyridylboronium units has been synthesised in almost quantitative yield.[16] Compound **C**, which possesses an unusual deep-purple colour due to charge-transfer interactions between the ferrocene backbone and its Diquat-like substituents,[15] acts as a fully reversible nine-electron redox system in DMF solution.[16] In an attempt to generate larger aggregates, we initially employed 1,1′-diborylated ferrocenes and bridging 2,2′-bipyridyl derivatives (e.g. quaterpyridine) with the hope of obtaining polymeric materials. However, macrocyclic dimers (e.g. **D**; Figure 1) always formed as the sole reaction products irrespective of the experimental conditions applied.[17] In our second approach, we tried to link ferrocene-1,1′-diylbis(2,2′-bipyridylboronium) cations via their boron atoms by introducing oxygen bridges between them. In contrast to our expectations, no polymeric species were formed but *ansa*-bridged complexes **E** (Figure 1) were obtained as the result of an intramolecular reaction.[12]

We therefore developed a new concept for the preparation of macromolecules containing larger numbers of 2,2′-bipyridylboronium cations and thus possessing the potential to act as electron storage media. Our synthetic methodology is based on a two-reaction sequence using a spontaneous B–N adduct formation in combination with a hydroboration reaction (Scheme 1).

To start, multiply borylated core units are required. Ferrocene and benzene are particularly well-suited candidates since they can easily be borylated up to four (ferrocene)[18] or up to three times (benzene).[19] In the present study, *p*-(dibromoboryl)toluene together with 1,4-bis- and 1,3,5-tris-(dibromoboryl)benzene will be employed. The other building blocks are 4,4′-bis(but-3′′-enyl)-2,2′-bipyridyl (**2**) and dibromoborane, $HBBr_2$, which may either be purchased as its dimethyl sulfide adduct or prepared in situ from tribromoborane and triethylsilane[20,21] in dichloromethane solution. In order to build the desired macromolecules, we will follow a divergent reaction sequence (Scheme 1): First, the

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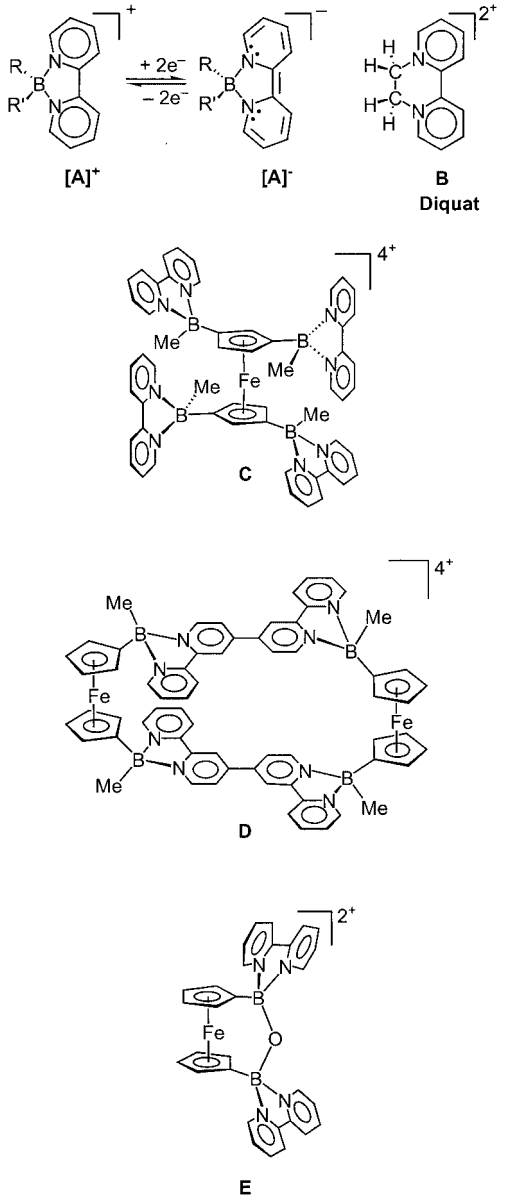
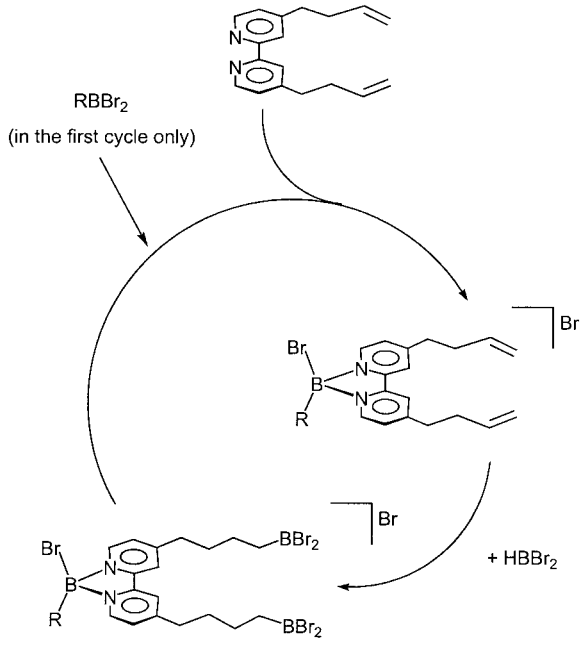


Figure 1. 2,2′-Bipyridylboronium cation (**A**), Diquat (**B**), ferrocene **C** bearing four 2,2′-bipyridylboronium substituents, macrocyclic dinuclear ferrocene complex **D**, and *ansa*-ferrocene **E**.

core unit is treated with the appropriate amount of substituted 2,2′-bipyridyl to prepare the zeroth generation (G_0) of the dendrimer. Second, the G_0 2,2′-bipyridylboronium cation is hydroborated with $HBBr_2$ at its peripheral olefin substituents to generate a molecule bearing alkyldibromoborane side-chains. In the third step, addition of the functionalised 2,2′-bipyridyl gives access to the G_1 dendrimer. The reaction cycle may then be repeated to attach further 2,2′-bipyridylboronium cations and to obtain higher generation dendrimers. The purpose of this paper is (i) to present an optimised procedure for the hydroboration of bipyridylboronium cations with olefinic side-chains, (ii) to prove that up to three bipyridylboronium substituents can be grouped around a benzene ring such that it qualifies as a core unit



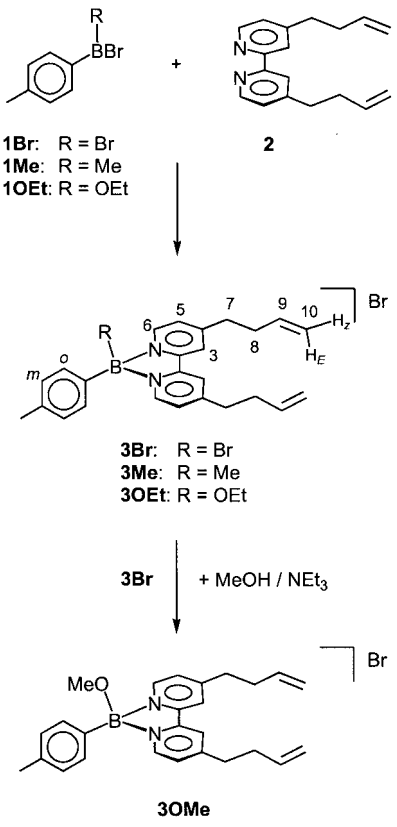
Scheme 1. Concept for the synthesis of branched 2,2′-bipyridylboronium cations by hydroboration with dibromoborane.

for further dendrimer syntheses, and (iii) to describe our first results regarding the synthesis of G_1 dendrimers.

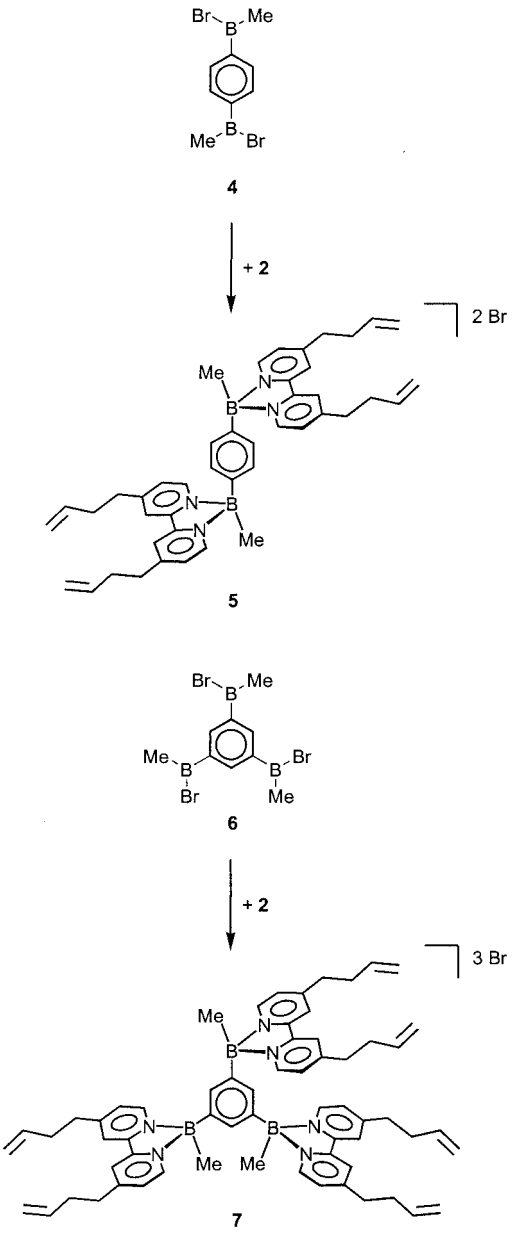
Results and Discussion

Syntheses

Treatment of *p*-(dibromoboryl)toluene (**1Br**)[19] with tetramethylstannane or diethyl ether gives *p*-[bromo(methyl)boryl]toluene (**1Me**) and *p*-[bromo(ethoxy)boryl]toluene (**1OEt**), respectively (Scheme 2). Addition of **1Br**, **1Me** or **1OEt** to the 2,2′-bipyridyl derivative **2**[22] in toluene or dichloromethane at ambient temperature leads to the formation of **3Br**, **3Me** and **3OEt**, respectively, in excellent yields. Compound **3Br**, bearing a bromo substituent at the boron atom, closely mimics the reaction intermediates encountered during the hydroboration/adduct formation cycle (cf. Scheme 1). However, B–Br bonds are prone to hydrolysis and it was therefore desirable to have also the moisture-stable methyl derivative **3Me** at hand. The ethoxy-2,2′-bipyridylboronium cation **3OEt** is described here because it gave crystals suitable for X-ray crystal structure analysis. Most importantly, the bromo substituent of **3Br** can be replaced by a methoxy group (**3OMe**; Scheme 2) when **3Br** is dissolved in dry methanol in the presence of stoichiometric amounts of triethylamine. This reaction proceeds cleanly and quantitatively, and thus offers a convenient way to transform the primary products of future dendrimer syntheses into air- and moisture-stable materials.



Scheme 2. Synthesis of the 2,2′-bipyridylboronium bromides **3Br**, **3Me**, **3OEt** and **3OMe**.



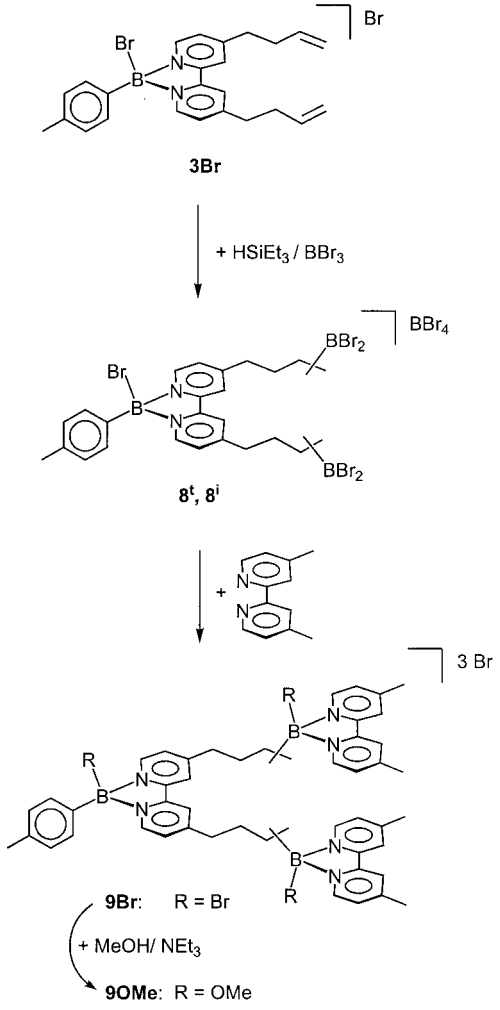
Scheme 3. Synthesis of the bis- and tris(2,2′-bipyridylboronium) bromides **5** and **7**.

The bromo(methyl)boryl-substituted benzenes **4** and **6**, which are accessible from $SnMe_4$ and 1,4-bis(dibromoboryl)benzene or 1,3,5-tris(dibromoboryl)benzene,[19] respectively, in a way similar to the synthesis of **1Me**, readily react with ligand **2** in dichloromethane to form the di- and trications **5** and **7**, respectively (Scheme 3). For purification, the reaction products were precipitated from their dichloromethane solutions by the addition of hexane.

The crucial hydroboration step was carried out using the bromo-substituted monocation **3Br**, since it is the least complex system available but nevertheless contains all the functional groups of a growing dendrimer according to Scheme 1. At the beginning we relied on $HBBr_2{\cdot}SMe_2$ as the hydroboration reagent, but it soon turned out that the in situ generation of $HBBr_2$ from equimolar amounts of triethylsilane and boron tribromide[20,21] gives better results. In the optimised procedure, a mixture of **3Br** and triethylsilane in dichloromethane is added dropwise at –78 °C to a solution of tribromoborane in the same solvent. The reaction is usually complete after warming to ambient temperature. Note that 3 equiv. of BBr_3 are required since 1 equiv. coordinates the bromide counterion of **3Br** to form tetrabromoborate $[BBr_4]^-$. As expected, the hydroboration of **3Br** is not fully regioselective such that isomers $\mathbf{8^t}$ (t = terminal) and $\mathbf{8^i}$ (i = internal) with a BBr_2 substituent attached to C-10 and C-9, respectively, are obtained [approx. ratio (^{1}H NMR spectroscopy): $\mathbf{8^t/8^i}$ = 4:1; see below] (Scheme 4). In order to increase the regioselectivity, we extended our studies to a derivative of **3Br** bearing methyl groups at both its C-9 atoms. In this case, however, C-9 becomes a chiral atom after hydroboration and a mixture of diastereomers is obtained.

Apart from the regioselectivity problem, the crude product **8** is sufficiently pure for further reaction with 2,2′-bipyridyls. A sample of **8** was thus treated with 4,4′-dimethyl-2,2′-bipyridyl in dichloromethane and subsequently with methanol/triethylamine to synthesise the G_1 trication **9OMe**. Attempts to isolate the regioisomers of **9OMe** by reversed-phase HPLC failed since a satisfactory separation could not be achieved.

As already mentioned above, tetrabromoborate is created as a new counterion in the hydroboration reaction. This causes additional problems, since $[BBr_4]^-$ reacts stoichio-



Scheme 4. Hydroboration of **3Br**, subsequent formation of the branched cation **9Br**, and transformation of **9Br** into the moisture-stable derivative **9OMe**.

metrically with 2,2′-bipyridyl similar to the alkyldibromoborane side-chains of **8**. As a consequence, the preparation of the first generation dendrimer **9Br** requires 3 rather than 2 equiv. of the ligand to achieve quantitative conversion. In our search for more suitable counterions, we finally found that $[B(C_6F_5)_4]^-$ is not affected by BBr_3/$HSiEt_3$, which makes it the counterion of choice for further dendrimer syntheses.

NMR Spectroscopy

The ^{11}B NMR shifts of the 2,2′-bipyridylboronium cations appear in the range between δ = 9.8 (**3OMe**) and 6.5 ppm (**3Br**, **7**), thus indicating the presence of tetracoordinate boron nuclei.[23] Very similar ^1H NMR spectra are observed for the monocations **3Br**, **3Me**, **3OEt** and **3OMe**. In all these compounds, the position of the H-3 resonance is strongly dependent on the nature of the counterion and the choice of solvent [cf. **3Me**: δ(H-3) = 10.31 (Br^-/$CDCl_3$), 8.87 (Br^-/CD_3OD), 7.16 ($[B(C_6H_5)_4]^-$/$CDCl_3$), 8.88 ppm ($[PF_6]^-$/$CDCl_3$)]. This effect may therefore be attributed to the formation of contact ion pairs, an interpretation also supported by the structure of **3OEt** in the solid state in which the two C-3–H-3 vectors act as "chelating hydrogen-bond donors" towards the bromide ion (corresponding H···Br contacts in the range between 2.80 and 3.00 Å (Figure 2; for the theoretical treatment of a related system, see ref.[24]). Hydroboration of **3Br** leads to the disappearance of the signals for the olefinic protons [δ(H-9) = 5.81, δ(H-10_E) = 5.05, δ(H-10_Z) = 4.99 ppm] and carbon atoms [δ(C-9) = 135.6, δ(C-10) = 117.1 ppm] and the appearance of new signals in the aliphatic region of the spectrum [**8^t**: δ(H-9) = 1.80, δ(H-10) = 1.71 ppm; δ(C9) = 26.4, δ(C-10) = 36.2 ppm]. Moreover, the ^{11}B NMR spectrum of **8** now reveals two resonances possessing chemical shift values typical of four- and three-coordinate boron nuclei [δ(Bbipy) = 6.5, δ(BBr_2) = 57.3 ppm; integral ratio ≈ 1:2]. Upon addition of 2 equiv. of 4,4′-dimethyl-2,2′-bipyridyl to **8**, the signal at δ = 57.3 ppm disappears and an extremely broad signal occurs at δ ≈ 7 ppm, which clearly shows that all former BBr_2 groups are now tetracoordinate.[23] There are three possible regioisomers of **9OMe**, containing between two and three different kinds of 2,2′-bipyridyl fragments. As a consequence, both the ^1H and the ^{13}C NMR spectra of **9OMe** are poorly resolved and very complex. It is therefore not possible to assign resonances to individual atoms

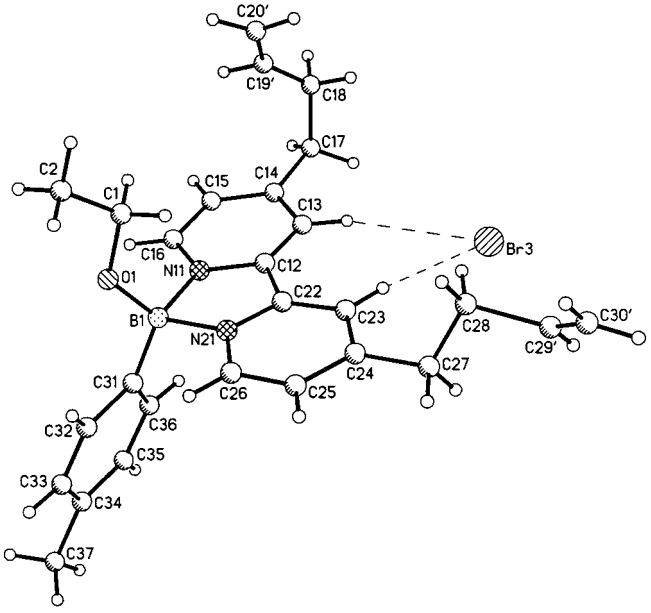


Figure 2. Ball-and-stick model of **3OEt** in the solid state. For clarity, only one of the three crystallographically independent molecules within the asymmetric unit is shown. Selected bond lengths [Å], angles [°] and torsion angles [°]: B(1)–O(1) 1.416(12), B(1)–C(31) 1.539(16), B(1)–N(11) 1.635(13), B(1)–N(21) 1.666(11), N(11)–C(12) 1.369(10), C(12)–C(22) 1.473(11), N(21)–C(22) 1.334(11); O(1)–B(1)–C(31) 114.7(8), O(1)–B(1)–N(11) 111.2(9), O(1)–B(1)–N(21) 110.2(7), C(31)–B(1)–N(11) 114.6(8), C(31)–B(1)–N(21) 111.9(8), N(11)–B(1)–N(21) 92.0(6), C(1)–O(1)–B(1) 123.1(8), C(12)–N(11)–B(1) 115.0(6), C(22)–N(21)–B(1) 113.9(7), N(11)–C(12)–C(22) 108.1(7), N(21)–C(22)–C(12) 110.8(7), C(13)–C(12)–C(22) 129.7(8), C(12)–C(22)–C(23) 127.1(8); N(11)–C(12)–C(22)–N(21) –3.4(12).

in this case. However, the proposed molecular structure of **9OMe** was clearly proven by mass spectrometry.

Mass Spectrometry

Low resolution electrospray mass spectra (ESI) in the positive-ion mode were recorded for the G_0 compounds **3Me**, **3OMe**, **3OEt**, **5** and **7**. The spectra of the 2,2′-bipyridylboronium salts **3Me**, **3OMe**, **3OEt** reveal exclusively peaks of the free monocations [**3Me** – Br]$^+$, [**3OMe** – Br]$^+$, and [**3OEt** – Br]$^+$ at *m*/*z* values of 381, 397 and 411, respectively. A similar result was obtained for the diborylated species **5**, which gave rise to only one peak assignable to the free dication [**5** – 2 Br]$^{2+}$ (*m*/*z* = 328). In the case of the trisubstituted benzene derivative **7**, two peaks with an integral ratio of 100 (*m*/*z* = 512):95 (*m*/*z* = 315) appear in the mass spectrum, which correspond to the di- and trications [**7** – 2 Br]$^{2+}$ and [**7** – 3 Br]$^{3+}$. An ESI mass spectrum was also recorded for **9OMe**. Again, the most intense peaks (*m*/*z* = 465, 284) by far may be assigned to the cations [**9OMe** – 2 Br]$^{2+}$ and [**9OMe** – 3 Br]$^{3+}$.

X-ray Crystallography

Single crystals of **3OEt** (triclinic, space group $P\bar{1}$) grew slowly from an oily sample at room temperature. There are three crystallographically independent molecules in the asymmetric unit. Since their structure parameters are equal within experimental error, the data of only one of the three molecules are discussed here. As already deduced from the NMR spectra, the compound contains a tetracoordinate boron centre chelated by a 2,2′-bipyridyl ligand [B(1)–N(11) = 1.635(13) Å, B(1)–N(21) = 1.666(11) Å; N(11)–B(1)–N(21) = 92.0(6)°]. Chelation of the small boron atom leads to a slight distortion of the 2,2′-bipyridyl moiety such that the angles C(13)–C(12)–C(22) and C(12)–C(22)–C(23) on the outer frame of the aromatic system are stretched to values of 129.7(8)° and 127.1(8)°, respectively. The terminal atoms C(19′), C(20′), C(29′) and C(30′) of the butenyl chains are disordered. Although a model with two different conformations has been employed, the anisotropic displacement parameters of C(19′) and C(20′) are still rather large.

Conclusions

This paper reports a novel strategy for the generation of dendritic macromolecules consisting of redox-active 2,2′-bipyridylboronium cations. 1,4-Di- and 1,3,5-triborylated benzenes are chosen as core units and a hydroboration/B–N adduct formation sequence is suggested for the assembly of the individual branches.

To prove the suitability of the benzene core unit, we first synthesised the air- and moisture-stable benzene derivatives **5** and **7** bearing two and three 4,4′-bis(but-3′′-enyl)-2,2′-bipyridylboronium substituents in their 1,4- and 1,3,5-positions. The reactions proceed cleanly and quantitatively, which leads to the conclusion that there is sufficient space along the periphery of a benzene ring to attach up to three branching subunits. Compounds **5** and **7** may therefore be regarded as generation zero (G_0) dendrimers.

In order to optimise the hydroboration reaction, the monocation **3Br**, derived from *p*-(dibromoboryl)toluene (**1Br**) and 4,4′-bis(but-3′′-enyl)-2,2′-bipyridyl (**2**), was employed as a model system. Quantitative conversion of both its olefinic side-chains into alkyldibromoboryl substituents was achieved under mild conditions with BBr_3/$HSiEt_3$ as hydroborating reagent. The regioselectivity of the hydroboration reaction is high (ratio of terminal vs. internal hydroboration ≈ 4:1). Introduction of methyl groups into the β-positions of the terminal alkenes eliminates the regioselectivity problem (NMR spectroscopic control) but leads to an inseparable mixture of diastereomers after hydroboration.

Apart from the fact that **8** was found to be a mixture of isomers **8**$^{\mathbf{t}}$ and **8**$^{\mathbf{i}}$, the sample obtained was sufficiently pure for further derivatisation with 4,4′-dimethyl-2,2′-bipyridyl. This reaction requires 3 rather than 2 equiv. of bipyridyl ligand; the third equivalent is consumed by the $[BBr_4]^-$ counterion of **8**. Bromo-substituted 2,2′-bipyridylboronium cations are sensitive towards hydrolysis, therefore **9Br** was transformed into the air- and moisture-stable derivative **9OMe** by treatment with methanol/triethylamine. The successful synthesis of **9OMe** was proven by ESI mass spectrometry.

Overall, the general synthetic concept outlined in this paper has successfully passed its first evaluation. However, the following modifications are required: (1) Despite numerous efforts, we have not been able to separate the different regioisomers of **9OMe** by HPLC or GPC techniques. Apart from the fact that the solubilities, polarities etc. of these isomers are obviously similar, the alkyl(bipyridyl)boronium cations within the dendrimer branches appear to be less stable than the aryl(bipyridyl)boronium cations formed with the core unit. We therefore decided to abandon the hydroboration step in future syntheses and to look for an alternative reaction that leads to more stable aryl(bipyridyl)-boronium ions and does not suffer from any regioselectivity problems. All these requirements are met by the system (trimethylsilyl)arene/BBr_3, which gives aryldibromoboranes and bromotrimethylsilane (in fact, this reaction has already been employed for the synthesis of our di- and triborylated core units[19]). Since we already have the 2,2′-bipyridyl derivative **10** (Figure 3) at our disposal,[22] there should be no major problem on switching from the hydroboration reaction to the Si/B exchange protocol. (2) During the hydro-

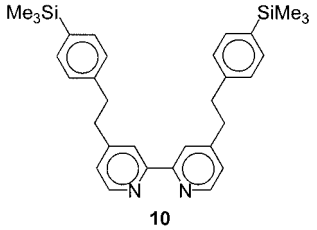


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Figure 3. 2,2′-Bipyridyl ligand **10** bearing 2-[(trimethylsilyl)aryl)]-ethyl groups.

boration step, a $[BBr_4]^-$ ion is created, which is reactive towards 2,2′-bipyridyls. Since the perfluorated tetraphenylborate anion $[B(C_6F_5)_4]^-$ turned out to be inert under the reaction conditions applied, it is advantageous to replace the Br^- ion by $[B(C_6F_5)_4]^-$ in future syntheses {e.g. by treatment with $Tl[B(C_6F_5)_4]$ or $Ag[B(C_6F_5)_4]$}.

Experimental Section

General Remarks: All reactions were carried out under oxygen-free argon or nitrogen using standard Schlenk techniques. Solvents were distilled under argon from sodium/benzophenone (toluene, *n*-hexane, *n*-pentane, triethylamine, methanol) or passed through a 4 Å molecular sieves column (CH_2Cl_2, $CHCl_3$) prior to use; the syntheses of *p*-(dibromoboryl)toluene (**1Br**),[19] 1,4-bis(dibromoboryl)benzene,[19] 1,3,5-tris(dibromoboryl)benzene[19] and 4,4′-bis(but-3′′-enyl)-2,2′-bipyridyl (**2**)[22] have been described elsewhere. NMR spectra were recorded with Bruker AMX 250, DPX 250 or Avance 400 spectrometers. Chemical shifts are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$); ^{11}B NMR chemical shifts are reported relative to external $BF_3{\cdot}Et_2O$. Low resolution electrospray mass spectra (ESI) were recorded in the positive-ion mode with a Fisons VG Platform II spectrometer.

1Me: Tetramethylstannane (4.699 g, 26.27 mmol) was added dropwise, at ambient temperature, to **1Br** (6.543 g, 25.00 mmol) in *n*-pentane (15 mL), and the mixture was stirred for 5 h. After the solvent had been evaporated, the residue was kept at 50 °C in vacuo for 3 h. Subsequent vacuum distillation gave pure **1Me** as a colourless liquid. Yield: 3.498 g (70%). ^1H NMR (250.1 MHz, $CDCl_3$, 25 °C): δ = 7.99 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, H-Ar$_o$), 7.25 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, H-Ar$_m$), 2.39 (s, 3 H, CH_3-Ar), 1.49 (s, 3 H, CH_3B) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$, 25 °C): δ = 70.5 ($h_{1/2}$ = 250 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 146.8 (C-Ar$_p$), 138.0 (C-Ar$_o$), 129.0 (C-Ar$_m$), 22.1 (CH_3-Ar) ppm; C-Ar$_i$, CH_3B not observed.

1OEt: Diethyl ether (1.495 g, 20.17 mmol) was added with a syringe to **1Br** (5.235 g, 20.00 mmol) in toluene (40 mL). After the solution had been stirred at room temperature for 5 d, the solvent was evaporated to give **1OEt** as an off-white oil, which was used without further purification. Yield: 3.993 g (88%). ^1H NMR (250.1 MHz, $CDCl_3$, 25 °C): δ = 8.16 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H-Ar), 7.13 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H-Ar), 4.18 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, OCH_2), 2.16 (s, 3 H, CH_3-Ar), 1.13 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$, 25 °C): δ = 38.4 ($h_{1/2}$ = 200 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 137.9, 135.9, 128.9 (C-Ar), 66.0 (OCH_2), 21.4 (CH_3-Ar), 16.1 (OCH_2CH_3) ppm; C-Ar$_i$ not observed.

3Br: A solution of **1Br** (0.393 g, 1.50 mmol) in toluene (2.5 mL) was added dropwise to a solution of **2** (0.397 g, 1.50 mmol) in toluene (5 mL). The reaction mixture immediately turned yellow and **3Br** precipitated as a yellow oil. This oil was isolated, washed with *n*-hexane and dried in vacuo to give the pure product as a yellow foam. Yield: 0.602 g (76%). ^1H NMR (250.1 MHz, $CDCl_3$, 25 °C): δ = 10.25 (br., 2 H, H-3), 8.45 (d, $^3J_{H,H}$ = 6.0 Hz, 2 H, H-6), 7.76 (dd, $^3J_{H,H}$ = 6.0, $^4J_{H,H}$ = 1.4 Hz, 2 H, H-5), 7.15 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, H-Ar$_o$), 7.09 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, H-Ar$_m$), 5.81 (ddt, $^3J_{H,H}$ = 17.1, 10.3, 6.6 Hz, 2 H, H-9), 5.05 (d, $^3J_{H,H}$ = 17.1 Hz, 2 H, H-10$_E$), 4.99 (d, $^3J_{H,H}$ = 10.3 Hz, 2 H, H-10$_Z$), 3.20 (t, $^3J_{H,H}$ = 7.4 Hz, 4 H, H-7), 2.67 (m, 4 H, H-8), 2.27 (s, 3 H, CH_3-Ar) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$, 25 °C): δ = 6.5 ($h_{1/2}$ = 400 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 164.7 (C-4), 144.6 (C-2), 142.3 (C-6), 140.0 (C-Ar$_p$), 135.6 (C-9), 132.2 (C-Ar$_o$), 129.4 (C-Ar$_m$), 129.0 (C-5), 126.8 (C-3), 117.1 (C-10), 35.3 (C-7), 33.1 (C-8), 21.2 (CH_3-Ar) ppm; C-Ar$_i$ not observed.

3Me: A solution of **1Me** (0.591 g, 3.00 mmol) in dichloromethane (5 mL) was added dropwise, at ambient temperature, to **2** (0.793 g, 3.00 mmol) in dichloromethane (10 mL). The solvent volume was reduced to approximately 5 mL and *n*-hexane added dropwise, whereupon **3Me** precipitated as a pale-yellow oil. Yield: 1.211 g (88%). ^1H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 10.31 (br., 2 H, H-3), 8.22 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, H-6), 7.59 (dd, $^3J_{H,H}$ = 5.9, $^4J_{H,H}$ = 1.4 Hz, 2 H, H-5), 7.06 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H-Ar$_m$), 6.91 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H-Ar$_o$), 5.85 (ddt, $^3J_{H,H}$ = 17.1, 10.3, 6.7 Hz, 2 H, H-9), 5.07 (d, $^3J_{H,H}$ = 17.1 Hz, 2 H, H-10$_E$), 5.01 (d, $^3J_{H,H}$ = 10.3 Hz, 2 H, H-10$_Z$), 3.20 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, H-7), 2.69 (m, 4 H, H-8), 2.27 (s, 3 H, CH_3-Ar), 0.61 (s, 3 H, CH_3B) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$, 25 °C): δ = 7.5 ($h_{1/2}$ = 350 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 161.5 (C-4), 145.1 (C-2), 141.3 (C-6), 138.1 (C-Ar$_p$), 135.7 (C-9), 131.1 (C-Ar$_o$), 129.0 (C-Ar$_m$), 128.3 (C-5), 125.3 (C-3), 116.5 (C-10), 34.8 (C-7), 33.2 (C-8), 20.9 (CH_3-Ar), 6.9 (CH_3B) ppm; C-Ar$_i$ not observed. ESI-MS: *m*/*z* (%) = 381 (100) [M^+ – Br]. $C_{26}H_{30}BBrN_2$ (461.25): calcd. C 67.70, H 6.56, N 6.07; found C 67.11, H 6.51, N 5.91.

3OEt: Compound **2** (2.247 g, 8.50 mmol) was dissolved in toluene (20 mL) and a solution of **1OEt** (1.929 g, 8.50 mmol) in toluene (20 mL) was added dropwise at ambient temperature, whereupon the reaction mixture became cloudy and the product precipitated as a red-brown oil. The solvent was decanted and the oil washed with *n*-hexane. Yield: 3.645 g (87%). ^1H NMR (250.1 MHz, $CDCl_3$, 25 °C): δ = 10.18 (br., 2 H, H-3), 8.27 (d, $^3J_{H,H}$ = 5.8 Hz, 2 H, H-6), 7.67 (dd, $^3J_{H,H}$ = 5.8, $^4J_{H,H}$ = 1.4 Hz, 2 H, H-5), 7.00 (m, 4 H, H-Ar), 5.81 (ddt, $^3J_{H,H}$ = 17.2, 10.3, 6.8 Hz, 2 H, H-9), 5.02 (d, $^3J_{H,H}$ = 17.2 Hz, 2 H, H-10$_E$), 4.96 (d, $^3J_{H,H}$ = 10.3 Hz, 2 H, H-10$_Z$), 3.17 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, H-7), 2.92 (q, $^3J_{H,H}$ = 6.9 Hz, 2 H, OCH_2), 2.65 (m, 4 H, H-8), 2.23 (s, 3 H, CH_3-Ar), 1.06 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, OCH_2CH_3) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$, 25 °C): δ = 9.1 ($h_{1/2}$ = 350 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 163.6 (C-4), 145.2 (C-2), 141.7 (C-6), 138.7 (C-Ar$_p$), 135.7 (C-9), 131.0 (C-Ar$_o$), 129.0 (C-Ar$_m$), 128.5 (C-5), 126.0 (C-3), 116.8 (C-10), 58.2 (OCH_2), 35.1 (C-7), 33.3 (C-8), 21.2 (CH_3-Ar), 17.4 (OCH_2CH_3) ppm; C-Ar$_i$ not observed. ESI-MS: *m*/*z* (%) = 411 (100) [M^+ – Br]. $C_{27}H_{32}BBrN_2O$ (491.27): calcd. C 66.01, H 6.57, N 5.70; found C 65.74, H 6.47, N 5.59.

3OMe: Compound **3Br** (0.789 g, 1.50 mmol) was dissolved in dry methanol (5 mL), treated with dry triethylamine (0.152 g, 1.50 mmol) from a syringe and the resulting reaction mixture was stirred at ambient temperature for 2 h. The solvent was evaporated and the residue dissolved in dichloromethane (5 mL). Addition of a few drops of *n*-hexane made the product precipitate as a light brown oil, which was isolated by decantation and washed with a mixture of dichloromethane and *n*-hexane. Yield: 0.635 g (89%). ^1H NMR (250.1 MHz, $CDCl_3$, 25 °C): δ = 10.18 (br., 2 H, H-3), 8.26 (d, $^3J_{H,H}$ = 5.8 Hz, 2 H, H-6), 7.67 (dd, $^3J_{H,H}$ = 5.8, $^4J_{H,H}$ = 1.5 Hz, 2 H, H-5), 7.02 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, H-Ar$_m$), 6.97 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, H-Ar$_o$), 5.81 (ddt, $^3J_{H,H}$ = 17.1, 10.4, 6.9 Hz, 2 H, H-9), 5.03 (d, $^3J_{H,H}$ = 17.1 Hz, 2 H, H-10$_E$), 4.97 (d, $^3J_{H,H}$ = 10.4 Hz, 2 H, H-10$_Z$), 3.18 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, H-7), 2.86 (s, 3 H, OCH_3), 2.66 (m, 4 H, H-8), 2.23 (s, 3 H, CH_3-Ar) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$, 25 °C): δ = 9.8 ($h_{1/2}$ = 400 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 163.7 (C-4), 145.2 (C-2), 141.7 (C-6), 138.8 (C-Ar$_p$), 135.7 (C-9), 131.0 (C-Ar$_o$), 129.0 (C-Ar$_m$), 128.6 (C-5), 126.0 (C-3), 116.8 (C-10), 50.4 (OCH_3), 35.1 (C-

7), 33.2 (C-8), 21.2 (CH_3-Ar) ppm; C-Ar_i not observed. ESI-MS: *m/z* (%) = 397 (100) [M^+ – Br]. $C_{26}H_{30}BBrN_2O$ (477.25): calcd. C 65.43, H 6.34, N 5.87; found C 64.80, H 6.33, N 5.62.

4: 1,4-Bis(dibromoboryl)benzene (2.295 g, 5.50 mmol) was dissolved in chloroform (15 mL) and tetramethylstannane (1.967 g, 11.00 mmol) was added dropwise at ambient temperature. The reaction mixture was stirred overnight, the solvent was evaporated, bromotrimethylstannane removed at 50 °C in vacuo, and the residue vacuum-sublimed to give pure **4** as a colourless solid. Yield: 0.854 g (54%). ^{1}H NMR (250.1 MHz, $CDCl_3$, 25 °C): δ = 8.14 (s, 4 H, H-Ar), 1.55 (s, 6 H, CH_3B) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 72.3 ($h_{1/2}$ = 400 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 135.5 (C-Ar) ppm; C-Ar_i, CH_3B not observed.

5: A solution of **4** (0.431 g, 1.50 mmol) in dichloromethane (5 mL) was added dropwise, at ambient temperature, to **2** (0.793 g, 3.00 mmol) in dichloromethane (10 mL). After the addition was complete, the solvent volume was reduced to approximately 5 mL and *n*-hexane added dropwise, which made **5** precipitate as a pale-yellow oil. Yield: 1.084 g (89%). ^{1}H NMR (250.1 MHz, $CDCl_3$, 25 °C): δ = 9.88 (br., 4 H, H-3), 8.31 (d, $^3J_{H,H}$ = 5.9 Hz, 4 H, H-6), 7.76 (dd, $^3J_{H,H}$ = 5.9, $^4J_{H,H}$ = 1.4 Hz, 4 H, H-5), 6.89 (s, 4 H, H-Ar), 5.81 (ddt, $^3J_{H,H}$ = 17.0, 10.3, 6.6 Hz, 4 H, H-9), 5.04 (d, $^3J_{H,H}$ = 17.0 Hz, 4 H, H-10$_E$), 4.98 (d, $^3J_{H,H}$ = 10.3 Hz, 4 H, H-10$_Z$), 3.15 (t, $^3J_{H,H}$ = 7.5 Hz, 8 H, H-7), 2.63 (m, 8 H, H-8), 0.58 (s, 6 H, CH_3B) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$, 25 °C): δ = 7.7 ($h_{1/2}$ = 580 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 161.8 (C-4), 145.2 (C-2), 141.4 (C-6), 135.9 (C-9), 131.5 (C-Ar), 128.6 (C-5), 125.5 (C-3), 116.9 (C-10), 35.1 (C-7), 33.4 (C-8) ppm; C-Ar_i, CH_3B not observed. ESI-MS: *m/z* (%) = 328 (100) [M^{2+} – 2 Br]. $C_{44}H_{50}B_2Br_2N_4$ (816.34): calcd. C 64.74, H 6.17, N 6.86; found C 64.29, H 6.07, N 6.66.

6: Preparation and purification was achieved as described for **4**. 1,3,5-Tris(dibromoboryl)benzene (2.348 g, 4.00 mmol), tetramethylstannane (2.217 g, 12.40 mmol), chloroform (20 mL). Yield: 0.674 g (43%). ^{1}H NMR (250.1 MHz, $CDCl_3$, 25 °C): δ = 9.02 (s, 3 H, H-Ar), 1.34 (s, 9 H, CH_3B) ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$, 25 °C): δ = 72.0 ($h_{1/2}$ = 350 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 149.0 (C-Ar) ppm; C-Ar_i, CH_3B not observed.

7: Compound **6** (0.863 g, 2.20 mmol) was dissolved in dichloromethane (10 mL) and added dropwise to a solution of **2** (1.718 g, 6.50 mmol) in dichloromethane (20 mL). The reaction mixture became yellow. After the addition was complete, *n*-hexane was added, which made **7** precipitate as a yellow oil. Yield: 2.086 g (80%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 8.89 (br., 6 H, H-3), 8.81 (d, $^3J_{H,H}$ = 5.9 Hz, 6 H, H-6), 8.13 (dd, $^3J_{H,H}$ = 5.9, $^4J_{H,H}$ = 1.3 Hz, 6 H, H-5), 6.62 (s, 3 H, H-Ar), 5.80 (ddt, $^3J_{H,H}$ = 17.1, 10.4, 6.6 Hz, 6 H, H-9), 5.05 (d, $^3J_{H,H}$ = 17.1 Hz, 6 H, H-10$_E$), 5.01 (d, $^3J_{H,H}$ = 10.4 Hz, 6 H, H-10$_Z$), 3.07 (m, 12 H, H-7), 2.56 (m, 12 H, H-8), 0.45 (s, 9 H, CH_3B) ppm. ^{11}B NMR (128.4 MHz, CD_3OD, 25 °C): δ = 6.5 ($h_{1/2}$ = 600 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 160.4 (C-4), 144.5 (C-2), 143.9 (C-6), 135.6 (C-9), 134.3 (C-Ar), 129.8 (C-5), 123.2 (C-3), 117.0 (C-10), 35.2 (C-7), 33.6 (C-8), 7.6 (CH_3B) ppm; C-Ar_i not observed. ESI-MS: *m/z* (%) = 512 (100) [M^{2+} – 2 Br], 315 (95) [M^{3+} – 3 Br]. $C_{63}H_{72}B_3Br_3N_6$ (1185.45): calcd. C 63.83, H 6.12, N 7.09; found C 63.39, H 6.08, N 6.85.

8: An intensely yellow solution of **3Br** (0.395 g, 0.75 mmol) and Et_3SiH (0.262 g, 2.25 mmol) in dichloromethane (5 mL) was added dropwise at –78 °C to BBr_3 (0.564 g, 2.25 mmol) in dichloromethane (5 mL) and the mixture then warmed to room temperature. Addition of *n*-hexane (5 mL) made **8** precipitate as a pale-yellow oil, which was isolated and vacuum-dried to give a colourless foam. According to the NMR spectra the conversion was quantitative. Major isomer **8^t**: ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 8.87 (s, 2 H, H-3), 8.60 (d, $^3J_{H,H}$ = 6.0 Hz, 2 H, H-6), 7.86 (dd, $^3J_{H,H}$ = 6.0, $^4J_{H,H}$ = 1.4 Hz, 2 H, H-5), 7.27 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H-Ar$_o$), 7.17 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H-Ar$_m$), 3.15 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, H-7), 2.32 (s, 3 H, CH_3-Ar), 1.94 (m, 4 H, H-8), 1.80 (m, 4 H, H-9), 1.71 (m, 4 H, H-10) ppm. ^{11}B NMR (126.8 MHz, CD_2Cl_2, 25 °C): δ = 57.3 (BBr_2, $h_{1/2}$ = 530 Hz), 6.5 (Bbipy, $h_{1/2}$ = 650 Hz), –24.1 ($[BBr_4]^-$, $h_{1/2}$ = 260 Hz) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 165.5 (C-4), 144.6 (C-2), 143.7 (C-6), 140.5 (C-Ar$_p$), 132.9 (C-Ar$_o$), 130.0 (C-5), 129.7 (C-Ar$_m$), 124.4 (C-3), 36.5 (C-7), 36.2 (C-10), 31.8 (C-8), 26.4 (C-9), 21.4 (CH_3-Ar) ppm; C-Ar_i not observed.

9OMe: Compound **8** (0.840 g, 0.75 mmol) was dissolved in dichloromethane (5 mL) and a solution of 4,4′-dimethyl-2,2′-bipyridyl (0.415 g, 2.25 mmol) in dichloromethane (5 mL) added dropwise with stirring. Upon addition, the solution adopted an intense yellow colour. After the reaction mixture had been stirred at ambient temperature for 2 h, the solvent was evaporated and the solid residue redissolved in methanol (5 mL). Et_3N (0.227 g, 2.25 mmol) was added with a syringe, the reaction mixture was stirred for 2 h, and the volatiles were removed in vacuo. All attempts to isolate **9OMe** from the solid residue obtained applying reversed-phase HPLC techniques [stationary phase: ReproSil-Pur C18-AQ (10 μm, 250 × 20 mm); eluent: methanol or methanol/acetonitrile] failed. However, ESI mass spectrometry proved the presence of **9OMe** in the crude product. ESI-MS: *m/z* = 284 [M^{3+} – 3 Br], 465 [M^{2+} – 2 Br].

Crystal Structure Determination: $C_{27}H_{32}BBrN_2O$, M = 491.27, triclinic, space group $P\bar{1}$, a = 13.154(2), b = 14.371(2), c = 23.377(5) Å, α = 87.329(15)°, β = 87.113(15)°, γ = 63.314(12)°, V = 3941.9(12) Å^3, Z = 6, D_c = 1.242 Mg m^{-3}, F(000) = 1536, Mo-K_α radiation (λ = 0.71073 Å), T = 173(2) K; crystal size 0.24 × 0.23 × 0.16 mm, ω-scan mode, measurement range ($-16 \le h \le 15$, $-17 \le k \le 17$, $-28 \le l \le 26$, $3.58 \le \theta \le 25.92$), 15100 independent reflections, μ = 1.584 mm^{-1}. The structure was solved by direct methods[25] and full-matrix least-squares refinement was carried out against F^2 using the SHELXL-97 program,[26] 905 parameters, R_1 = 0.1833 (all data), wR_2 = 0.2230 (all data), max./min. residual electron density +0.580/–0.512 e Å^{-3}. CCDC-271402 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: May 9, 2005
Published Online: September 21, 2005

