

(3 × 10 mL), and dried under high vacuum to yield the desired 1,2-diimine resins **4**. These resins were then split and converted into the corresponding complexes of Ni<sup>II</sup> (**5**) and Pd<sup>II</sup> (**6**) by the addition of [(dme)NiBr<sub>2</sub>] (30 mg, 0.10 mmol) or [(cod)PdMeCl] (27 mg, 0.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and the reaction block was shaken for 12 h. The resins were then washed with CH<sub>2</sub>Cl<sub>2</sub> (4 × 10 mL) and dried under high vacuum to afford the desired resin-bound complexes. Loading capacities for these resins were calculated to be approximately 0.30 mmol g<sup>-1</sup> based on Ni and Pd analysis.

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## Dendritic Pseudorotaxanes\*\*

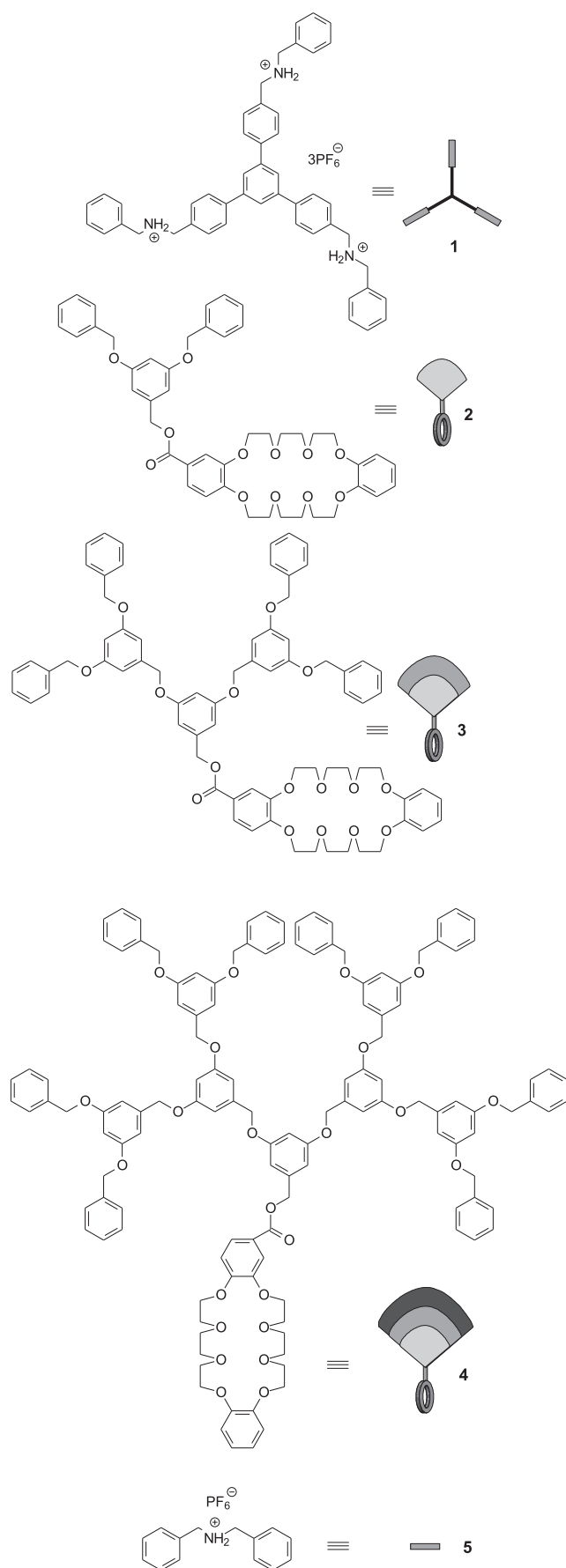
Nori Yamaguchi, Lesley M. Hamilton, and Harry W. Gibson\*

While dendrimers begin to find their potential applications in the fields of molecular electronics,<sup>[1]</sup> material science (high-performance polymers, catalysts, adhesives, etc.),<sup>[2]</sup> and membrane chemistry,<sup>[3]</sup> structural control<sup>[4]</sup> and synthetic efficiency still remain the major issues in dendrimer research. Three synthetic methods (convergent,<sup>[5]</sup> divergent,<sup>[6]</sup> and double-stage convergent<sup>[7]</sup>) are recognized, up to now, for the preparation of high molecular weight, monodisperse dendrimers. Recently, Zimmerman and Feng introduced a synthetic approach based on self-organization, which guarantees structural accuracy while eliminating steps from the conventional multistep approach.<sup>[8]</sup> In this case, six subunits were brought together by hydrogen bonding to construct supramolecular dendritic structures up to the fourth generation. Here, we report a concise self-organizing dendrimer synthesis in which 1:3 pseudorotaxane complexes between a triply charged ammonium salt (**1**)<sup>[9]</sup> (Scheme 1) and substituted dibenzo[24]crown-8 (DB24C8) units make up the core portions of the dendritic architectures. This is based on the finding of Stoddart et al. that DB24C8 forms pseudorotaxanes with secondary ammonium salts through noncovalent bonding.<sup>[10]</sup>

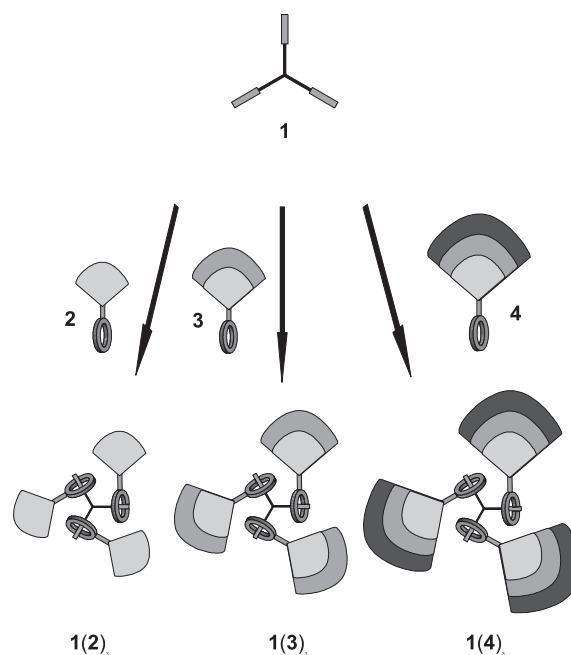
The cyclization reaction between tri(ethylene glycol) dichloride and methyl 3,4-dihydroxybenzoate at high dilution gave 4-methoxycarbonyldibenzo[24]crown-8 in 40% yield. The ester group was hydrolyzed and then esterified with a series of benzyl ether dendrons bearing primary alcohol moieties ([G1]-OH, [G2]-OH, and [G3]-OH)<sup>[5]</sup> using the redox system diethyl azodicarboxylate (DEAD) and triphenylphosphane (TPP)<sup>[11]</sup> to afford the corresponding dendrons with the macrocyclic unit at the focal points (**2–4**; Scheme 1). Our strategy to construct a series of self-organizing dendrimers is illustrated in Scheme 2.

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Scheme 1. Cartoon representations of the tritopic salt **1**, [G1]-DB24C8 (**2**), [G2]-DB24C8 (**3**), and [G3]-DB24C8 (**4**), and the monotopic salt **5**.



Scheme 2. Schematic illustrations of the construction of a series of self-organizing dendritic pseudorotaxanes from complementary building blocks.

The first evidence of formation of the 1:3 dendritic pseudorotaxanes from **1** and the series of dendrons **2–4** in solution came from  $^1\text{H}$  NMR spectrometry. In the case of the third-generation dendritic pseudorotaxane, when a  $3.0 \times 10^{-2}\text{M}$  solution of **4** in  $[\text{D}]\text{chloroform}$  was mixed with 1/3 molequiv of solid **1**, the  $^1\text{H}$  NMR spectrum of the mixture displayed signals associated with the complexed ammonium salt moiety of **1**, complexed **4**, and uncomplexed **4** on the basis of slow association and dissociation on the  $^1\text{H}$  NMR time scale (Figure 1). A gradual dissolution of otherwise insoluble **1** with increasing mixing time was evidenced by the appearance of

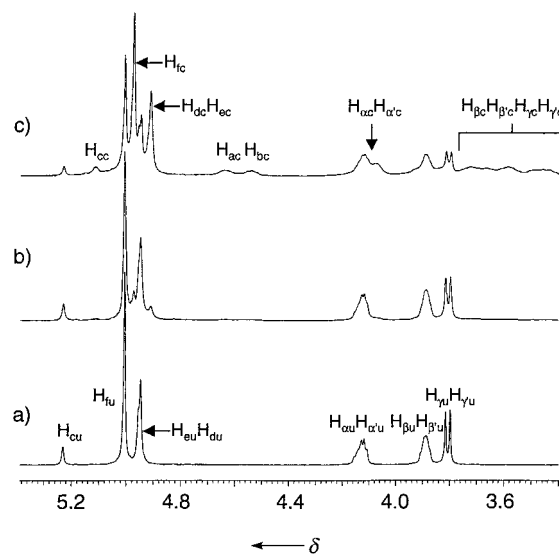
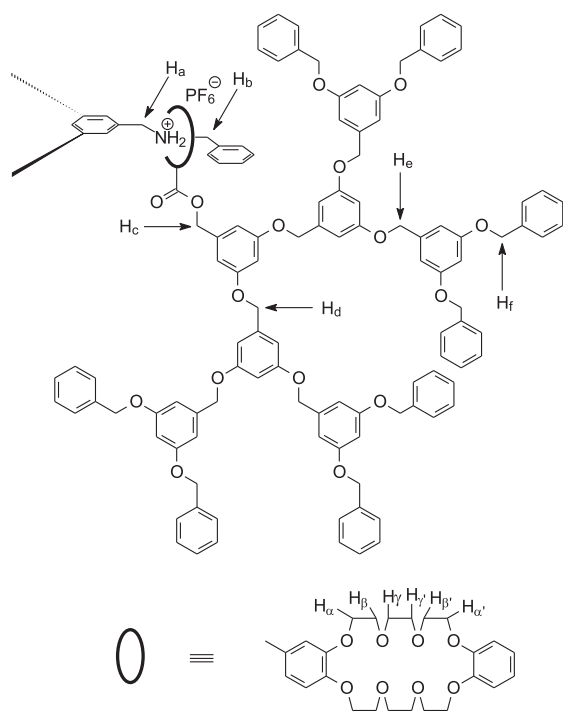


Figure 1. The aliphatic region of stacked  $^1\text{H}$  NMR spectra (400 MHz,  $[\text{D}]\text{chloroform}$ ,  $21.8^\circ\text{C}$ ) of a  $3.0 \times 10^{-2}\text{M}$  solution of **4** (a) and a  $3.0 \times 10^{-2}\text{M}$  solution of **4** mixed with 1/3 molequiv of solid **1** recorded after 10 min (b) and 72 h (c).

the new signals for  $H_{ac}$  and  $H_{bc}$  of the complexed ammonium salt moiety of **1** (Scheme 3) and their gradual increase in intensity. The stoichiometry of the complex was determined to be 1:3 by simple integration of the signals for relevant protons since the signals for  $H_{au}$  and  $H_{bu}$  of the uncomplexed ammonium salt moiety of **1** were undetected, indicating the absence of the 1:1 and 1:2 complexes in chloroform. Ammonium salt **1** was taken into solution slowly (dissolution of 17, 57, and 59% after 10 min, 48 h, and 72 h, respectively), and the complexation process finally reached equilibrium after 72 h.

The slow formation of dendritic pseudorotaxane **1(4)**<sub>3</sub> is presumably due to a combination of the poor solubility of **1** and steric hindrance experienced by neighboring dendron units in the 1:3 complex. The latter can be explained by the following two spectroscopic observations. 1) Significant up-field chemical shifts (Figure 1) were observed for the complexed benzylic protons  $H_{cc}$ ,  $H_{dc}$ ,  $H_{ec}$ , and  $H_{fc}$  of **4** in **1(4)**<sub>3</sub> (see Scheme 3). By contrast, the <sup>1</sup>H NMR spectra of a  $1.0 \times 10^{-2}$  M solution of **4** in [D]chloroform mixed with 1 molequiv of solid dibenzylammonium hexafluorophosphate (**5**), which were recorded periodically with increasing mixing time, were identical and showed that the signals for the benzylic protons



Scheme 3. The designation of the benzylic protons in **1** and **4** for the signal assignments in Figure 1.

of **4** in the 1:1 complex **4(5)** were not distinguishable from those of uncomplexed **4**.<sup>[12]</sup> 2) Similar <sup>1</sup>H NMR experiments for the formation of the dendritic pseudorotaxanes **1(2)**<sub>3</sub> and **1(3)**<sub>3</sub> in [D]chloroform revealed that complexation equilibrium was reached more quickly when the dendron units were less bulky (after 36 and 48 h, respectively).

Gel permeation chromatography (GPC) is routinely used for analyzing dendrimers, but accurate determination of molecular weight is difficult even with the principle of the

universal calibration due to the low hydrodynamic volume of dendrimers.<sup>[5]</sup> In the present case in chloroform at 25 °C **1(4)**<sub>3</sub> apparently dissociates in the column; only **4** elutes and salt **1** is retained in the column.

Mass spectrometry has been utilized increasingly in the characterization of dendrimers through the use of fast atom bombardment (FAB),<sup>[13]</sup> electron spray ionization (ESI),<sup>[14]</sup> and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) techniques.<sup>[15]</sup> By these analytical methods mass accuracies are in the range of 0.0027–0.10%. The application of these techniques was thus extended to the self-organized dendritic pseudorotaxanes. The third-generation dendritic pseudorotaxane **1(4)**<sub>3</sub> was characterized by MALDI-TOF-MS because of its high mass.<sup>[16]</sup> The spectrum (Figure 2) was dominated by three peaks which correspond to 1:3, 1:2, and 1:1 complexes.<sup>[17]</sup> The wholly complexed

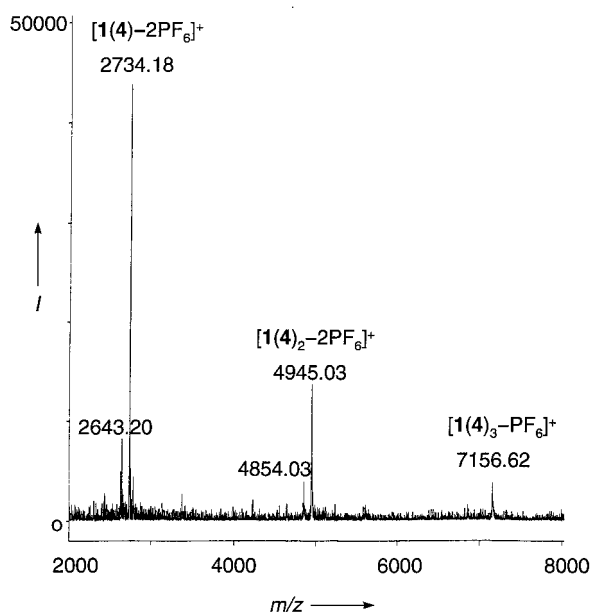


Figure 2. The MALDI-TOF mass spectrum of the third-generation dendritic pseudorotaxane **1(4)**<sub>3</sub>. The spectrum was measured in the positive-ion mode using 2,5-dihydroxybenzoic acid as the matrix and acetone as the solvent. *I* = signal intensity in counts.

dendritic pseudorotaxane **1(4)**<sub>3</sub> was detected at  $m/z$  7156.62 after loss of  $PF_6^-$ . The 1:2 and 1:1 complexes give rise to the peaks at  $m/z$  4945.03 and 2734.18, respectively. The lower abundance side peaks at  $m/z$  4854.03 and 2643.2 are found at regular intervals from  $[1(4)_2 - 2PF_6]^+$  and  $[1(4) - 2PF_6]^+$  ( $\Delta(m/z)$  91.00 and 90.98, respectively), indicating loss of benzyl groups from the periphery of the dendrons. The calculated and observed masses (<0.1% error) of the self-organized dendritic pseudorotaxanes **1(2)**<sub>3</sub>, **1(3)**<sub>3</sub>, and **1(4)**<sub>3</sub> are summarized in Table 1.

We have designed and constructed various generations of self-organizing pseudorotaxane dendrimers concisely and efficiently. The <sup>1</sup>H NMR investigations in [D]chloroform indicated formation of the self-organizing dendritic pseudorotaxanes as a result of a simple recognition between the secondary ammonium salt moieties in **1** and dibenzo[24]-crown-8 units at the focal points of the dendron units. Mass

Table 1. Molecular formulae, calculated molecular masses, and observed (MS) mass/charge ratios of the supramolecular structures.

Structure	Molecular formula	Calcd mass	Obs <i>m/z</i>
<b>1(2)</b> <sub>3</sub> – PF <sub>6</sub> <sup>[a]</sup>	C <sub>48</sub> H <sub>48</sub> N <sub>3</sub> P <sub>2</sub> F <sub>12</sub> (C <sub>46</sub> H <sub>50</sub> O <sub>12</sub> ) <sub>3</sub>	3339.3	3339.5
<b>1(2)</b> <sub>2</sub> – 2 PF <sub>6</sub> <sup>[a]</sup>	C <sub>48</sub> H <sub>48</sub> N <sub>3</sub> PF <sub>6</sub> (C <sub>46</sub> H <sub>50</sub> O <sub>12</sub> ) <sub>2</sub>	2400.0	2400.2
<b>1(2)</b> <sub>3</sub> – 3 PF <sub>6</sub> <sup>[a]</sup>	C <sub>48</sub> H <sub>48</sub> N <sub>3</sub> (C <sub>46</sub> H <sub>50</sub> O <sub>12</sub> ) <sub>3</sub>	1460.7	1459.2
<b>1(3)</b> <sub>3</sub> – PF <sub>6</sub> <sup>[b]</sup>	C <sub>48</sub> H <sub>48</sub> N <sub>3</sub> P <sub>2</sub> F <sub>12</sub> (C <sub>74</sub> H <sub>74</sub> O <sub>16</sub> ) <sub>3</sub>	4611.81	4611.06
<b>1(3)</b> <sub>2</sub> – 2 PF <sub>6</sub> <sup>[b]</sup>	C <sub>48</sub> H <sub>48</sub> N <sub>3</sub> PF <sub>6</sub> (C <sub>74</sub> H <sub>74</sub> O <sub>16</sub> ) <sub>2</sub>	3248.34	3248.69
<b>1(3)</b> <sub>3</sub> – 2 PF <sub>6</sub> <sup>[b]</sup>	C <sub>48</sub> H <sub>48</sub> N <sub>3</sub> PF <sub>6</sub> (C <sub>74</sub> H <sub>74</sub> O <sub>16</sub> ) <sub>2</sub>	1884.88	1884.90
<b>1(4)</b> <sub>3</sub> – PF <sub>6</sub>	C <sub>48</sub> H <sub>48</sub> N <sub>3</sub> P <sub>2</sub> F <sub>12</sub> (C <sub>130</sub> H <sub>122</sub> O <sub>24</sub> ) <sub>3</sub>	7156.81	7156.62
<b>1(4)</b> <sub>2</sub> – 2 PF <sub>6</sub>	C <sub>48</sub> H <sub>48</sub> N <sub>3</sub> PF <sub>6</sub> (C <sub>130</sub> H <sub>122</sub> O <sub>24</sub> ) <sub>2</sub>	4945.01	4945.03
<b>1(4)</b> <sub>3</sub> – 2 PF <sub>6</sub>	C <sub>48</sub> H <sub>48</sub> N <sub>3</sub> PF <sub>6</sub> (C <sub>130</sub> H <sub>122</sub> O <sub>24</sub> ) <sub>2</sub>	2733.22	2734.18

[a] The FAB mass spectrum of the first-generation dendritic pseudorotaxanes was recorded in the positive-ion mode with 3-nitrobenzyl alcohol as the matrix and acetone as the solvent. [b] The FAB mass spectrum of the second-generation dendritic pseudorotaxanes was measured in the positive-ion mode with *trans*-3-indoleacrylic acid as the matrix and THF as the solvent.

spectrometry was also used to characterize the self-organized dendritic pseudorotaxanes. Space-filling (CPK) models of **1(2)**<sub>3</sub>, **1(3)**<sub>3</sub>, and **1(4)**<sub>3</sub> show ball-shaped aggregates with diameters of approximately 8, 10, and 12 nm, respectively. This approach based on self-organization offers the possibility of generating even larger and more complex supramolecular dendrimers.

## Experimental Section

**4-Methoxycarbonyldibenzo[24]crown-8:** To a 5-L three-necked, round-bottomed flask equipped with a mechanical stirrer, N<sub>2</sub> inlet, and a thermometer were added DMF (3.5 L), *n*Bu<sub>4</sub>NI (100 mg), and K<sub>2</sub>CO<sub>3</sub> (80.60 g, 584 mmol), and the mixture was heated to 110 °C. A solution of *o*-bis(8-chloro-3,6-dioxooctyloxy)benzene (25.4 g, 61.8 mmol) and methyl 3,4-dihydroxybenzoate (10.4 g, 61.8 mmol) in DMF (120 mL) was added by syringe pump at the rate of 0.75 mL h<sup>−1</sup>. After the addition was complete the reaction mixture was vigorously stirred for 3 d, cooled to 25 °C, and filtered through celite. The solvent was removed to give a brown viscous liquid. This was preabsorbed onto silica gel and the product was continuously extracted with Et<sub>2</sub>O using a Soxhlet extraction apparatus. After the solvent was removed, the resulting yellow solid was recrystallized from EtOH to give a white powder (12.5 g, 39.8% yield). M.p. 83–85 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.84 (8H, m), 3.87 (3H, s), 3.93 (8H, m), 4.15 (4H, t, *J* = 8.0 Hz), 4.19 (4H, t, *J* = 8.0 Hz), 6.84 (1H, d, *J* = 8.4 Hz), 6.88 (4H, m), 7.52 (1H, d, *J* = 2.0 Hz), 7.64 (1H, dd, *J* = 2.0, 8.4 Hz); low-resolution (LR) FAB-MS: *m/z*: 506.2 [M]<sup>+</sup>, 475.2 [M – OCH<sub>3</sub>]<sup>+</sup>; high-resolution (HR) FAB-MS: calcd for [M]<sup>+</sup> C<sub>26</sub>H<sub>34</sub>O<sub>10</sub>: 506.2152; found: 506.2132; elemental analysis calcd for C<sub>26</sub>H<sub>34</sub>O<sub>10</sub>: C 61.67, H 6.77; found: C 61.75, H 6.80.

**4-Carboxydibenzo[24]crown-8:** A 250-mL one-necked, round-bottomed flask was charged with 4-methoxycarbonyldibenzo[24]crown-8 (3.16 g, 6.24 mmol) and EtOH (100 mL). A solution of aqueous KOH (4M, 10 mL) was added dropwise and the reaction mixture was heated at reflux for 12 h. Upon completion of the reaction the solvent was removed to give an off-white solid, which was redissolved in H<sub>2</sub>O (100 mL) and neutralized with H<sub>2</sub>SO<sub>4</sub>. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 100 mL), and the organic layers were combined, dried over MgSO<sub>4</sub>, and concentrated to give a white solid, which was recrystallized from EtOH to give a white solid (2.73 g, 88.9% yield). M.p. 182–183 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.84 (8H, m), 3.93 (8H, m), 4.15 (4H, t, *J* = 4.0 Hz), 4.20 (4H, t, *J* = 4.0 Hz), 6.88 (5H, m), 7.56 (1H, d, *J* = 1.6 Hz), 7.71 (1H, dd, *J* = 1.6, 8.4 Hz); LR FAB-MS: *m/z*: 531.1 [M + K]<sup>+</sup>, 492.2 [M]<sup>+</sup>; HR FAB-MS: calcd for [M]<sup>+</sup> C<sub>25</sub>H<sub>32</sub>O<sub>10</sub>: 492.1995; found: 492.1985; elemental analysis calcd for C<sub>25</sub>H<sub>32</sub>O<sub>10</sub>: C 60.97, H 6.55; found: C 61.19, H 6.60.

**General procedure for 2–4:** A 25-mL round-bottomed flask equipped with a magnetic stirrer was charged with the appropriate dendritic benzyl alcohol ([G1]-OH, [G2]-OH, or [G3]-OH)<sup>[5]</sup> (1.00 equiv), 4-carboxydiben-

zo[24]crown-8 (1.00 equiv), TPP (1.50 equiv), and THF. DEAD (1.50 equiv) was added dropwise by syringe, and the reaction mixture was stirred at 25 °C for 10 h. The solvent was evaporated to give a white solid (a yellow viscous liquid in the cases of **3** and **4**), which was passed through a short column of silica gel with EtOAc as the eluent. The resulting white solid (colorless viscous liquid in the cases of **3** and **4**) was redissolved in EtOAc and precipitated into MeOH to afford a white solid (a clear glass in the cases of **3** and **4**).

[G1]-DB24C8 (**2**): 84% yield; m.p. 113–114 °C (MeOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.84 (8H, m), 3.93 (8H, m), 4.15 (4H, m), 4.20 (4H, m), 5.04 (4H, s), 5.26 (2H, s), 6.59 (1H, t, *J* = 2.0 Hz), 6.67 (2H, d, *J* = 2.0 Hz), 6.84 (1H, d, *J* = 8.8 Hz), 6.88 (4H, m), 7.30–7.43 (10H, m), 7.55 (1H, d, *J* = 2.0 Hz), 7.67 (1H, dd, *J* = 2.0, 8.8 Hz); LR FAB-MS: *m/z*: 794.4 [M]<sup>+</sup>; HR FAB-MS: calcd for [M]<sup>+</sup> C<sub>46</sub>H<sub>50</sub>O<sub>12</sub>: 794.3302; found: 794.3300; elemental analysis calcd for C<sub>46</sub>H<sub>50</sub>O<sub>12</sub>: C 69.51, H 6.34; found: C 69.43, H 6.31.

[G2]-DB24C8 (**3**): 89% yield, colorless glass; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.82 (8H, m), 3.91 (8H, m), 4.13–4.18 (8H, m), 4.97 (4H, s), 5.02 (8H, s), 5.25 (2H, s), 6.55 (1H, t, *J* = 2.0 Hz), 6.56 (2H, t, *J* = 2.0 Hz), 6.65 (2H, d, *J* = 2.0 Hz), 6.67 (4H, d, *J* = 2.0 Hz), 6.81 (1H, d, *J* = 8.4 Hz), 6.84–6.90 (4H, m), 7.31–7.41 (20H, m), 7.54 (1H, d, *J* = 2.0 Hz), 7.65 (1H, dd, *J* = 2.0, 8.4 Hz); LR FAB-MS: *m/z*: 1218.6 [M]<sup>+</sup>; HR FAB-MS: calcd for [M]<sup>+</sup> C<sub>74</sub>H<sub>74</sub>O<sub>16</sub>: 1218.4977; found: 1218.4943; elemental analysis calcd for C<sub>74</sub>H<sub>74</sub>O<sub>16</sub>: C 72.89, H 6.12; found: C 72.82; H 6.10.

[G3]-DB24C8 (**4**): 93% yield, colorless glass; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.81 (m, 8H), 3.89 (m, 8H), 4.13 (m, 8H), 4.95 (s, 12H), 5.01 (s, 16H), 5.23 (s, 2H), 6.53 (t, 2H, *J* = 2.4 Hz), 6.56 (t, 4H, *J* = 2.4 Hz), 6.58 (t, 1H, *J* = 2.4 Hz), 6.66 (m, 14H), 6.80 (d, 1H, *J* = 8.4 Hz), 6.87 (m, 4H), 7.28–7.41 (m, 40H), 7.54 (s, 1H), 7.64 (d, 2H, *J* = 8.4 Hz); LR FAB-MS: *m/z*: 2090.9 [M + Na]<sup>+</sup>; HR FAB-MS: calcd for [M + Na]<sup>+</sup> C<sub>130</sub>H<sub>122</sub>O<sub>24</sub>Na 2090.8257; found: 2090.8227.

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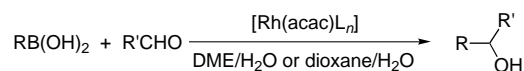
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## Rhodium-Catalyzed Addition of Organoboronic Acids to Aldehydes

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The transmetalation between organo/main group metal reagents and transition metal compounds is of great importance for application in organic synthesis, since it allows the formation of new carbon–carbon bonds between various organometallic units and electrophiles. We previously demonstrated the efficiency of transmetalation between boron and palladium in the cross-coupling reaction of organoboron compounds with organic electrophiles<sup>[1]</sup> and the transmetalation between boron and rhodium in the catalytic 1,4-addition of aryl- or 1-alkenylboronic acids to enones.<sup>[2]</sup> An analogous

addition reaction of organotin compounds to enones<sup>[3]</sup> and to aldehydes<sup>[4]</sup> has recently appeared. Here we report our first attempts to extend the protocol to the addition of aryl- and 1-alkenylboronic acids to aldehydes in an aqueous solution (Scheme 1). The insertion of carbonyl groups into transition metal–carbon bonds has not received much attention, but the use of transition metals as catalysts may allow addition of organometallics that are otherwise inert,<sup>[5]</sup> asymmetric addition using a chiral phosphane complex,<sup>[6]</sup> or reaction in an aqueous phase.



Scheme 1. Rhodium-catalyzed addition of organoboronic acids to aldehydes. R = aryl, 1-alkenyl; R' = alkyl, aryl.

A combination of  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (acac = acetylacetonate) and a phosphane ligand in an aqueous solvent, conditions that gave good results for the 1,4-addition of organoboronic acids to enones,<sup>[2]</sup> was also effective for the addition to aldehydes (Table 1). The reaction was induced by phosphane complexes having a large P–Rh–P angle,<sup>[7a]</sup> which

Table 1. Effect of ligand and solvent on the addition of phenylboronic acid to 4-methoxybenzaldehyde in the presence of  $[\text{Rh}(\text{acac})(\text{CO})_2]$ .<sup>[a]</sup>

Entry	Ligand	Solvent	Yield [%] <sup>[b]</sup>
1	3 Ph <sub>3</sub> P	DME/H <sub>2</sub> O	0
2	3 Ph <sub>3</sub> As	DME/H <sub>2</sub> O	< 1
3	3 Cy <sub>3</sub> P	DME/H <sub>2</sub> O	5
4	dppe <sup>[c]</sup>	DME/H <sub>2</sub> O	0
5	dppp <sup>[d]</sup>	DME/H <sub>2</sub> O	82 (79)
6	dppb <sup>[e]</sup>	DME/H <sub>2</sub> O	17
7	diop <sup>[f]</sup>	DME/H <sub>2</sub> O	66
8	dppf <sup>[g]</sup>	DME/H <sub>2</sub> O	99 (83)
9	dppf <sup>[g]</sup>	dioxane/H <sub>2</sub> O	72
10	dppf <sup>[g]</sup>	nPrOH/H <sub>2</sub> O	84

[a] A mixture of 4-MeOC<sub>6</sub>H<sub>4</sub>CHO (1 mmol), PhB(OH)<sub>2</sub> (2 mmol) and  $[\text{Rh}(\text{acac})(\text{CO})_2]$ /ligand (3 mol %) was stirred at 80 °C for 16 h in solvent/H<sub>2</sub>O (1/1) (6 mL). [b] GC yields based on the aldehyde and yields of the isolated product are given in the parentheses. [c] 1,2-Bis(diphenylphosphanyl)ethane. [d] 1,3-Bis(diphenylphosphanyl)propane. [e] 1,4-Bis(diphenylphosphanyl)butane. [f] 2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphanyl)butane. [g] 1,1'-Bis(diphenylphosphanyl)ferrocene.

may affect the rate of carbonyl insertion into the Rh–C bond.<sup>[7b–d]</sup> Thus, monodentate phosphanes and dppe were totally ineffective ligands (entries 1–4), but the complexes derived from dppp, diop, and dppf exhibited high catalytic activity (entries 5, 7, and 8). However, the ligand dppb unexpectedly resulted in a low yield although it has a similar bite angle (entry 6). The reaction smoothly proceeded in aqueous 1,2-dimethoxyethane (DME), dioxane, and propanol at temperatures above 80 °C (entries 9 and 10), but it was very slow in the absence of water or at temperatures below 80 °C.

Representative results are summarized in Table 2. The reaction is rather sensitive to electronic effects both in aldehydes and arylboronic acids, suggesting that the mechanism proceeds through the nucleophilic attack of the aryl group to the carbonyl. Thus, the reaction was facilitated in the

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