

## An Unusual Oligomerization/Oxidation Reaction of a 3-Boron-Substituted 1-Phenyl-1,3-Butadiene Produces a Hexameric Product.

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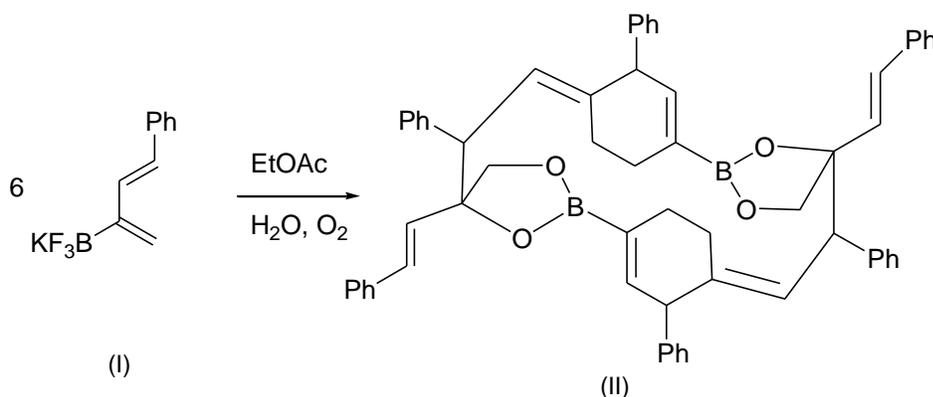
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An unusual hexameric structure has been isolated from exposure of 3-BF<sub>3</sub>-1-Phenyl-1,3-Butadiene to air and moisture in an attempt to obtain crystals of the starting compound.

Formation of this hexamer is rationalized and its structural features are compared to other B(OR)<sub>2</sub> substituted cyclohexane and benzene ring containing structures.

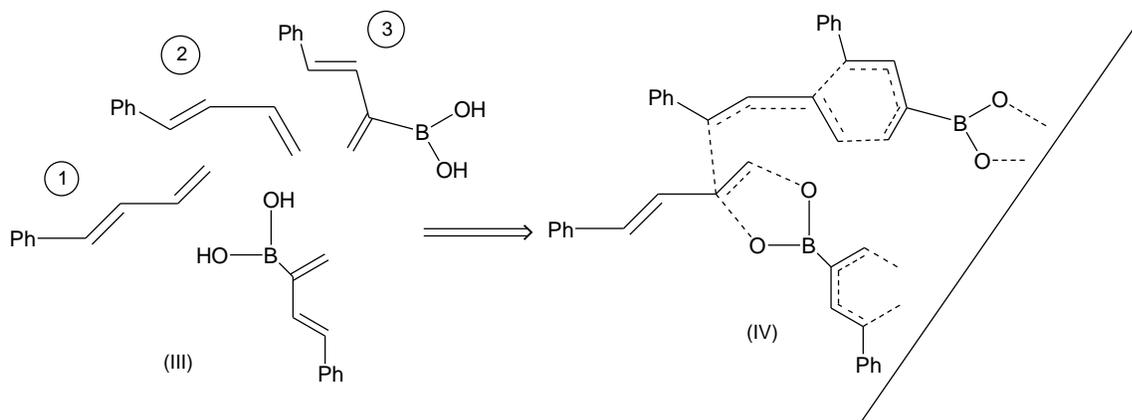
### Comment

We have recently begun to prepare 2-boron- (De and Welker, 2005) and 2-silicon-substituted 1,3-dienes and investigate their Diels-Alder/Cross coupling reactions (Pidaparathi, Day, and Welker, 2007). Most recently, we reported the preparation of several halogen substituted phenylbutadienes and their conversion into boron substituted dienes (De, Day, and Welker, 2007). To our surprise, when we attempted to grow crystals of BF<sub>3</sub> substituted diene (I) in ethyl acetate under atmospheric conditions we isolated a symmetrical structure (II) derived from 6 molecules of (I).



We can rationalize the formation of (II) through drawings (III) and IV). The rationalization requires protonolysis of some of the boron carbon bonds in (I) to generate some 1-phenyl-1,3-

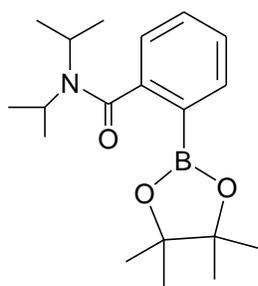
butadiene. The terminal double bond of one 1-phenyl-1,3-butadiene molecule (labeled 1 in figure III below) appears to have been oxidized and to have participated in an electrophilic addition reaction with the internal alkene of a second molecule of 1-phenyl-1,3-butadiene (labeled 2 in figure III below). The terminal double bond of this second molecule of 1-phenyl-1,3-butadiene has participated in a Diels-Alder reaction with a boron substituted diene (depicted as the boronic acid substituted diene 3 in figure III below). The rationalization shown also requires a hydrolysis of the starting dienyl trifluoroborate (I). Organotrifluoroborates are known to hydrolyze easily in mildly basic acetone/water mixtures (Yuen and Hutton, 2005). We suspect there may still be traces of methoxide present after the preparation of (I) and this catalyzes the hydrolysis required by the production of (II).



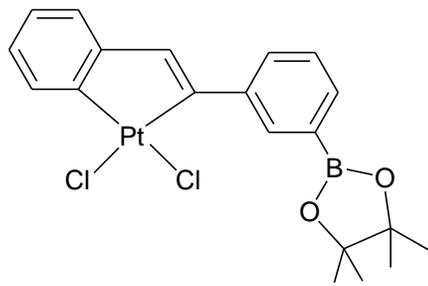
The molecular structure of compound (II) is depicted in Figure 1 and selected geometric parameters are given in Table 1. Bond lengths of note in or near the boron atom's coordination sphere are C3-B1 1.553(4), B1-O1 1.361(4), B1-O2 1.369(4), C3-C4 1.322(4), O1-C1 1.454(3), and O2-C2 1.455(3) Å. Bond angles of note that include, or are near to the boron atoms, are C4-C3-B1 118.6(3), C8-C3-B1 119.7(3), C3-B1-O1 123.7(3), C3-B1-O2 123.0(3), O1-B1-O2 113.3(3), B1-O1-C1 108.2(2), and B1-O2-C2 106.6(2)°. The C3-B1 bonds in this structure are similar to other  $sp^2$  C-boron bonds in boronate ester compounds that have been reported recently

(V-VII) [1.555-1.588 Å; (V) Coghlan et. al., 2005; (VI) Darwish et. al., 2004; (VII) Pohl et. al., 2004]. Likewise the B-O bond lengths and C-O bond lengths here are in the range of those reported previously [1.35-1.38 Å; Coghlan et. al., 2005; Darwish et. al., 2004; Pohl et. al., 2004] and 1.45-1.47 Å; Coghlan et. al., 2005; Darwish et. al., 2004; Pohl et. al., 2004]. With respect to bond angles, the O-B-O bond angles in this structure and other related ones are all  $113 \pm 1^\circ$  (Coghlan et. al., 2005; Darwish et. al., 2004; Pohl et. al., 2004). The C-C-B bond angles are all  $119 \pm 1^\circ$  and the C-B-O bond angles are all  $123 \pm 1^\circ$  (Coghlan et. al., 2005; Darwish et. al., 2004; Pohl et. al., 2004).

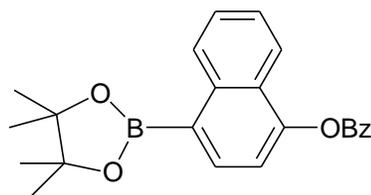
There are no accessible voids in the hexamer (II). The styryl (C15-C16-Ph) group appears to be where it is for steric reasons. The contacts which support this assertion involve the hydrogen on C15 (H15) and H2a (2.649 Å) (vanderWaals is 2.4) and H15 and aromatic ring carbon atoms C25 (2.786 Å) and C30 (3.013 Å) (vanderWaals is 2.9). Any rotation of the styryl (C15C16-Ph) group to minimize the short H16...O1 (2.392 Å) contact would result in a shorter H15 to H2a contact or a shorter H15 to aromatic ring contact depending upon the direction of rotation.



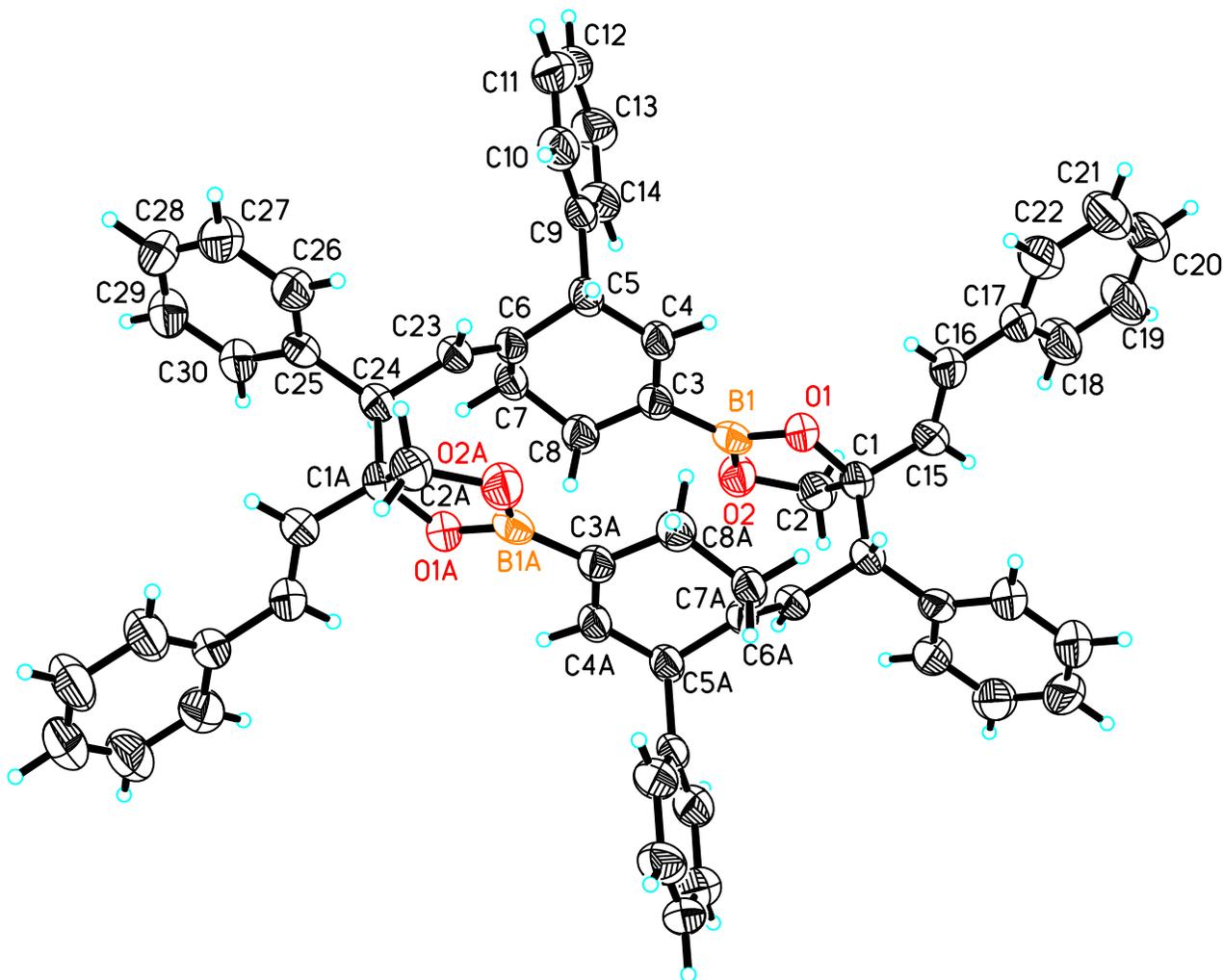
(V)



(VI)



(VII)



**Figure 1**

The molecular structure of (II). All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily-small spheres, which are in no way representative of their true thermal motion.

## Experimental

Complex (I) (3-BF<sub>3</sub>-1-Phenyl-1,3-butadiene) was prepared as described previously (De, Day, and Welker, 2007). Crystals of II were grown by evaporation of an ethyl acetate/acetone solution of (I) at 298°K with no precautions taken to exclude air. Colorless plate-shaped crystals of C<sub>60</sub>H<sub>54</sub>B<sub>2</sub>O<sub>4</sub> are, at 193(2) K, monoclinic, space group P2<sub>1</sub>/n [an alternate setting of P2<sub>1</sub>/c – C<sub>2h</sub><sup>5</sup> (No. 14)] with a = 13.212(3) Å, b = 6.0975(13) Å, c = 29.028(6) Å, β = 101.764(3)°, V = 2289.3(8) Å<sup>3</sup> and Z = 2 molecules {d<sub>calcd</sub> = 1.249 g/cm<sup>3</sup>; μ<sub>a</sub>(MoKα) = 0.076 mm<sup>-1</sup>}. A full

hemisphere of diffracted intensities (1868 30-second frames with a  $\omega$  scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Bruker SMART APEX CCD Single Crystal Diffraction System. X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 1350 reflections. A total of 13447 integrated reflection intensities having  $2\theta(\text{MoK}\alpha) < 46.52^\circ$  were produced using the Bruker program SAINT; 3260 of these were unique and gave  $R_{\text{int}} = 0.082$  with a coverage which was 99.3% complete. The Bruker software package SHELXTL was used to solve the structure using “direct methods” techniques. All stages of weighted full-matrix least-squares refinement were conducted using  $F_o^2$  data with the SHELXTL Version 6.10 software package.

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The hydrogen atoms were included in the structural model as idealized atoms (assuming  $sp^2$ - or  $sp^3$ -hybridization of the carbon atoms and C-H bond lengths of 0.95 – 1.00  $\text{\AA}$ ). The isotropic thermal parameters of all hydrogen atoms were fixed at values 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. A total of 298 parameters were refined using no restraints, 3260 data and weights of  $w = 1 / [\sigma^2(F^2) + (0.0438 P)^2]$ , where  $P = [F_o^2 + 2F_c^2] / 3$ . Final agreement factors at convergence are:  $R_1(\text{unweighted, based on } F) = 0.048$  for 1769 independent “observed” reflections having  $2\theta(\text{MoK}\alpha) < 46.52^\circ$  and  $I > 2\sigma(I)$ ;  $R_1(\text{unweighted, based on } F) = 0.095$  and  $wR_2(\text{weighted, based on } F^2) = 0.107$  for all 3260 independent reflections having  $2\theta(\text{MoK}\alpha) < 46.52^\circ$ . The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.16 and -0.15  $e^- / \text{\AA}^3$ , respectively.

*Crystal data*

Identification code	a7912m
Empirical formula	C60 H54 B2 O4
Formula weight	860.65
Temperature	193(2) K
Wavelength	0.71073 $\text{\AA}$

Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n [an alternate setting of P2 <sub>1</sub> /c – C <sub>2h</sub> <sup>5</sup> (No. 14)]
Unit cell dimensions	a = 13.212(3) Å b = 6.0975(13) Å, β = 101.764(3) ° c = 29.028(6) Å
Volume	2289.3(8) Å <sup>3</sup>
Z	2
Density (calculated)	1.249 g/cm <sup>3</sup>
Absorption coefficient	0.076 mm <sup>-1</sup>
F(000)	912
Crystal size	0.37 x 0.09 x 0.03 mm <sup>3</sup>
Theta range for data collection	3.82 to 23.26°
Index ranges	-14 ≤ h ≤ 14, -6 ≤ k ≤ 6, -32 ≤ l ≤ 31
Reflections collected	13447
Independent reflections	3260 [R(int) = 0.0824]
Completeness to theta = 23.26°	99.3 %
Absorption correction	None
Max. and min. transmission	0.9977 and 0.9725
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / parameters	3260 / 298
Goodness-of-fit on F <sup>2</sup>	0.850
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0478, wR <sub>2</sub> = 0.0949
R indices (all data)	R <sub>1</sub> = 0.0946, wR <sub>2</sub> = 0.1074
Largest diff. peak and hole	0.164 and -0.147 e <sup>-</sup> /Å <sup>3</sup>

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$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

**Table 1.**

Selected Bond lengths [Å] and angles [°] for C<sub>60</sub>H<sub>54</sub>B<sub>2</sub>O<sub>4</sub>

O(1)-B(1)	1.361(4)	O(2)-B(1)	1.369(4)
O(1)-C(1)	1.454(3)	O(2)-C(2)	1.455(3)
B(1)-C(3)	1.553(4)		
C(1)-C(15)	1.496(3)	C(3)-C(8)	1.496(3)

C(4)-C(5)	1.506(3)	C(23)-C(24)	1.511(3)
C(5)-C(6)	1.520(3)	C(24)-C(25)	1.529(4)
C(5)-C(9)	1.528(3)		
C(6)-C(7)	1.488(4)		
C(1)-C(2)	1.528(4)	C(7)-C(8)	1.532(3)
C(1)-C(24)#1	1.558(3)		
C(3)-C(4)	1.322(4)		
B(1)-O(1)-C(1)	108.2(2)	B(1)-O(2)-C(2)	106.6(2)
O(1)-B(1)-O(2)	113.3(3)	O(2)-B(1)-C(3)	123.0(3)
O(1)-B(1)-C(3)	123.7(3)		
O(1)-C(1)-C(15)	109.7(2)		
C(4)-C(3)-B(1)	118.6(3)		
C(8)-C(3)-B(1)	119.7(3)		

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MEW wishes to acknowledge the National Science Foundation for the funding of this research and the purchase of the X-ray equipment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: ). Services for accessing these data are described at the back of this journal.

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