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Ring Expansion Reactions of Pentaphenylborole with Dipolar Molecules as a Route to Seven-Membered Boron Heterocycles

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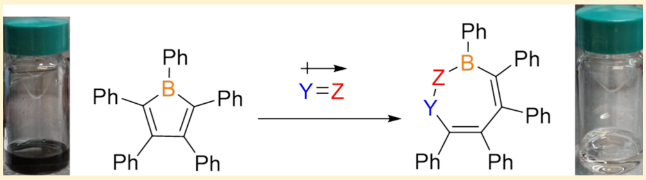
Supporting Information



ABSTRACT: Reactions of pentaphenylborole with isocyanates, benzophenone, and benzaldehyde produced new seven-membered heterocycles in high yields. For 1-adamantyl isocyanate, a BNC_5 heterocycle was obtained from the insertion of the C−N moiety into the five-membered borole, whereas for 4-methoxyphenyl isocyanate, a BOC_5 heterocycle was generated from the insertion of the C−O unit. These reactions are believed to occur via a mechanism wherein coordination of the nucleophile to the borole (1-adamantyl, N-coordination or O-coordination for 4-methoxyphenyl) is followed by ring expansion to afford the observed seven-membered heterocycles. The selectivity to form B−O- or B−N-containing heterocycles is based on the polarization of the isocyanate implying tunable reactivity for the system. Having observed that isocyanates react as 1,2-dipoles with pentaphenylborole, we examined benzophenone and benzaldehyde, which both reacted to insert C−O units into the ring. This represents a new efficient method for preparing rare seven-membered boracycles.

INTRODUCTION

In recent years, boron-containing unsaturated heterocycles have gained considerable attention for their interesting electronic properties.[1−10] However, few routes have been developed for the synthesis of boron heterocycles, which has hindered progress in this field. In search of new synthetic methods for boracycles, we were attracted to the five-membered heterocycle borole as a reagent to generate larger ring systems. Although pentaphenylborole (**I**) was first prepared 45 years ago by Eisch, its reactivity remained virtually undeveloped until recently.[11−14] In the past few years, there has been a resurgence in borole chemistry spearheaded by Piers,[15−26] Braunschweig,[27−51] and others advancing the chemistry of these fascinating species.[52−71]

Boroles exhibit antiaromatic character with powerful Lewis acidity at the boron center.[46] In many cases, borole adducts can be labile engaging in further reactivity (Figure 1). Braunschweig et al. showed that upon photolysis, the 2,6-lutidine borole complex (**1**) shifts the Lewis base from the boron to the adjacent carbon atom (**2**), which thermally converts back to the boron adduct.[33] In an example demonstrating the ability of boroles to act as reagents for new heterocycle synthesis, Piers showed that the reaction of carbon monoxide with **I** (Eisch's borole) results in the coordination of the carbonyl (**3**) followed by ring expansion to form the six-membered ring **4**.[20] Only the coordination complex forms at low temperatures, and the binding of CO is reversible; the ring expansion reaction requires warming to room temperature to overcome the energetic barrier to form **4**. Interestingly, the more electrophilic perfluorinated analogue (Piers' borole, **II**, Figure 2) does not endure the ring expansion.

For Piers' borole, reactivity proceeding via the coordination of diphenylacetylene to the Lewis acidic boron center was observed.[16] The coordination complex subsequently goes through an aryl migration and a ring expansion to also yield a six-membered ring system (**5**) as the major product. The minor product is a borepin (**6**) resulting from a Diels−Alder pathway. Alternatively, the cycloaddition product is exclusively formed with Eisch's borole.[13]

Recently, Braunschweig et al. reported the reaction of azides with Eisch's borole to provide expedient access to 1,2-azaborines (for example **8**).[47] Subsequently, we were able to isolate the kinetically favored product, an eight-membered BN_3C_4 heterocycle as a borole adduct (**7**).[72] Theoretical investigations indicated that the mechanism proceeds initially by the coordination of the α-nitrogen of the azide to the borole and ultimately inserts the α-nitrogen atom into the ring expelling N_2. Bettinger et al. showed that a similar nitrogen atom insertion occurs in 9-borafluorene species (**III**).[61,66] An amino-substituted derivative can rearrange to the azaborine complex **9**, and the azido-9-borafluorene thermally eliminates N_2 to incorporate a nitrogen atom into the ring to generate the *B,N*-phenanthryne **10**, which undergoes tetramerisation.

On the basis of these findings, we envisioned that this ring-expansion chemistry, particularly from an initial coordination complex, could be effective with other unsaturated small molecules. Herein, we examine the reactivity of isocyanates with borole **I**. After observing that isocyanates inserted into the borole as a 1,2-dipole, we turned our attention to carbonyl compounds, which reacted in a similar fashion. The results

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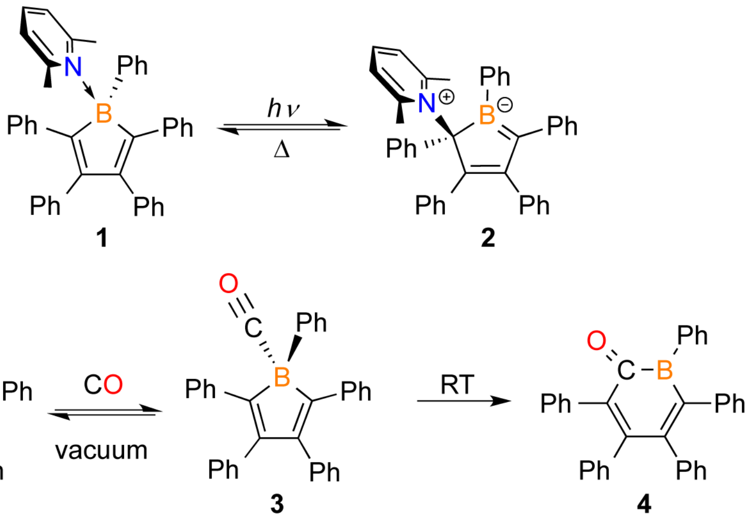


Figure 1. Reactions illustrating the lability of borole adducts.

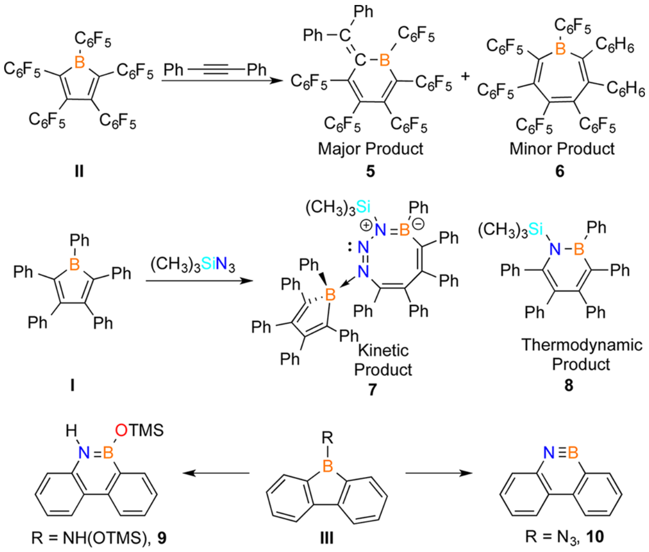


Figure 2. Reactions of boroles with diphenylacetylene and trimethylsilyl azide as well as insertion chemistry with 9-borafluorene.

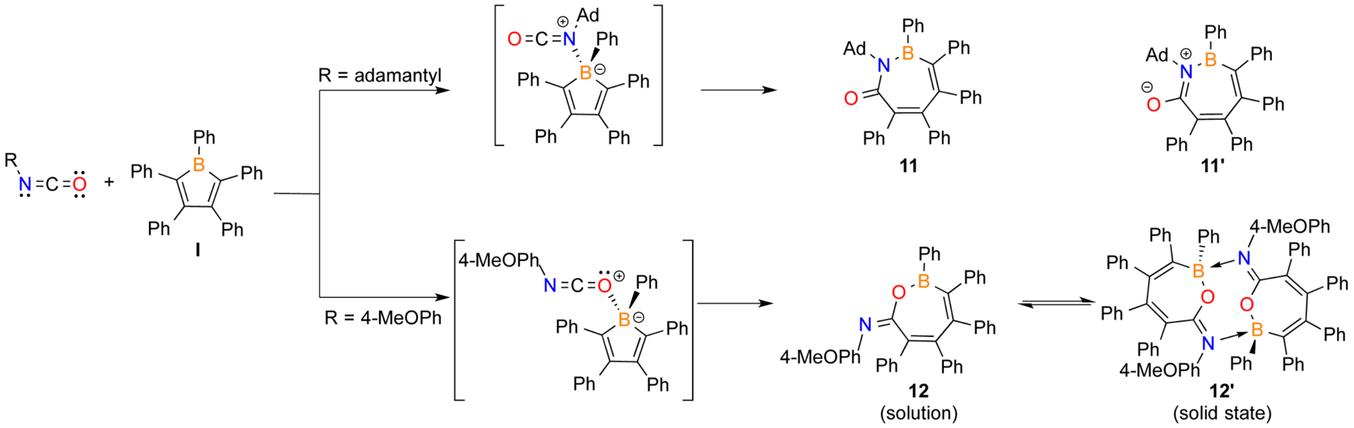
presented define an efficient method for the synthesis of new seven-membered boron heterocycles.

■ RESULTS AND DISCUSSION

The 1:1 reaction of 1-adamantyl isocyanate with Eisch's borole in toluene at room temperature immediately resulted in the loss of the deep blue color of the borole (Scheme 1). Removing the solvent in vacuo gave a white solid, which was washed with hexanes and dried in vacuo. Redissolving the solids in $CDCl_3$ and obtaining a ^1H NMR spectrum revealed one species with the aryl resonances from the borole integrating in a 25:15 ratio to the adamantyl peaks of the isocyanate, consistent with a 1:1 reaction with the product isolated in an 81% yield. Crystals suitable for an X-ray diffraction study were grown from a diethyl ether solution via vapor diffusion into hexanes. The solid-state structure reveals the product as the seven-membered BNC_5 heterocycle **11** formed from the insertion of the C−N moiety of the isocyanate into the ring (Figure 3, Table 1). This observed ring expansion to a seven-membered ring differs from the borole chemistry with trimethylsilyl azide that proceeded to an eight-membered ring and subsequently converted to the six-membered 1,2-azaborine (**7** and **8**).[47,72]

The endocyclic B−N bond distance of 1.498(2) Å in **11** is slightly shorter than a typical single bond, whereas the endocyclic B−C distance of 1.576(2) Å is in the range of a typical B−C single bond. The boron center is essentially planar [sum of angles about B = 359.9(1)°] as expected for a three-

Scheme 1. Reactions of I with 1-Adamantyl Isocyanate and 4-Methoxyphenyl Isocyanate to Generate Boracycles 11 and 12



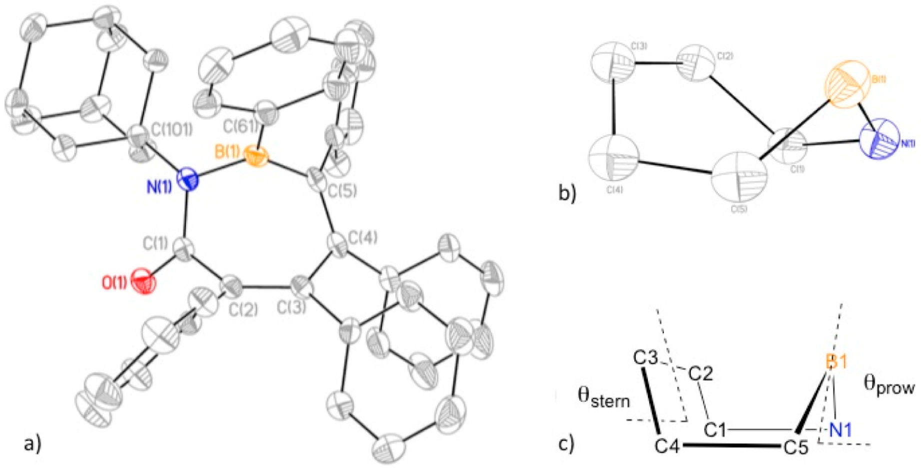


Figure 3. (a) Solid-state structure of **11**. Hydrogen atoms were omitted for clarity. Ellipsoids were drawn at the 50% probability level. Selected bond lengths (Å): B(1)−N(1) 1.498(2), N(1)−C(1) 1.367(2), C(1)−O(1) 1.222(2), C(1)−C(2) 1.526(2), C(2)−C(3) 1.351(2), C(3)−C(4) 1.493(2), C(4)−C(5) 1.352(2), C(5)−B(1) 1.576(2), B(1)−C(61) 1.550(2). Selected bond angles and dihedral angles (deg): N(1)−B(1)−C(61) 123.1(1), N(1)−B(1)−C(5) 112.6(1), C(5)−B(1)−C(61) 124.2(1), C(101)−N(1)−B(1)−C(61) 78.7(2). (b) View of the seven-membered ring; (c) Diagram illustrating the dihedral planes ϑ_{prow} and ϑ_{stern} defining the deviation of the ring from planarity into a boat-like conformation. Selected dihedral planes (deg): ϑ_{prow} 61.7(1), ϑ_{stern} 51.5(1).

Table 1. Crystallographic Data for 11−14

compound	**11**	**12′**	**13**	**14**
empirical formula	$C_{45}H_{40}BNO$	$C_{84}H_{64}B_2N_2O_4$	$C_{41}H_{31}BO$	$C_{47}H_{35}BO$
CCDC	1 032 439	1 032 440	1 032 442	1 032 441
FW (g/mol)	621.59	1186.99	550.51	626.56
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	P/c
a (Å)	10.7271(8)	13.5669(7)	12.8212(16)	10.3111(3)
b (Å)	14.1716(10)	14.1590(7)	15.808(2)	15.8416(5)
c (Å)	14.6970(11)	18.4513(9)	16.9423(19)	11.7030(4)
α (deg)	65.813(2)	81.2260(10)	100.047(4)	90
β (deg)	81.033(2)	78.651(2)	103.508(4)	115.1120(10)
γ (deg)	87.040(2)	65.2790(10)	109.228(4)	90
V (Å^3)	2013.0(3)	3146.8(3)	3032.0(6)	1730.93(10)
Z	2	2	4	2
D_c (Mg m^{-3})	1.026	1.253	1.207	1.202
radiation, λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
temp (K)	150(2)	150(2)	150(2)	150(2)
$R1[I > 2\sigma I]^a$	0.0522	0.0685	0.0830	0.0398
$wR2(F^2)^a$	0.1325	0.1629	0.2449	0.0764
GOF $(S)^a$	1.055	1.022	1.118	1.027

$^a R1(F[I > 2(I)]) = \sum||F_0| - |F_c||/\sum|F_0|$; $wR2(F^2\ [\text{all data}]) = [w(F_0^2 - F_c^2)^2]^{1/2}$; S (all data) $= [w(F_0^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_0^2) + (aP)^2 + bP]$, where $P = (F_0^2 + 2F_c^2)/3$, and a and b are constants suggested by the refinement program.

coordinate boron. The exocyclic carbon−oxygen bond clearly exhibits double bond character [1.222(2) Å], and the corresponding stretch was also observed in the Fourier transform infrared (FT-IR) spectrum at 1642 cm^{-1} as expected for an amido group. The seven-membered ring is nonplanar, with both B1 and C2/C3 rising out of the plane defined by N1−C1−C4−C5; the angles between this plane and those defined by N1/B1/C5 and C1/C2/C3/C4 (θ_{prow} and θ_{stern}, see Figure 3c) are 61.7(1)° and 51.5(1)°, respectively. There is distinct bond length alternation within the ring, with C2−C3 and C4−C5 exhibiting shorter distances than the C1−C2 and C3−C4 bond lengths. Collectively, these data rule out a delocalized aromatic resonance structure (**11′**), which could be drawn as a borepin analogue.[9,73,74] This BNC_5 heterocyclic motif is rare, as only three other such compounds have been structurally characterized, all of the others having saturated substituents around the boron center.[75−78] In solution compound **11** is stable at room temperature but decomposed upon heating.[79]

The mechanism is believed to occur first via coordination of the nitrogen atom of the isocyanate to the boron center followed by a subsequent ring expansion to the electrophilic carbon atom of the isocyanate to form the seven-membered ring. This reaction can be formally viewed as the insertion of a 1,2-dipole into the borole heterocycle. The reaction products imply that a cycloaddition with the butadiene framework of the borole is not observed.

To explore the chemistry with an aryl variant, 4-methoxyphenyl isocyanate was reacted with 1 equiv of borole **I** in CH_2Cl_2. After the addition, the blue borole solution

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became colorless. Removing the volatiles in vacuo, washing the solids with hexanes, and drying afforded an off-white powder. Redissolving the powder in $CDCl_3$ and obtaining a ^1H NMR spectrum revealed a single resonance for the methoxy group (δ = 3.65 ppm) integrating in a 3:29 ratio to the aryl protons, indicating a 1:1 reaction with the product isolated in an 82% yield. An X-ray diffraction study was performed on crystals grown from a diethyl ether solution via vapor diffusion into hexanes (Figure 4, **12′**) showing that the solid-state structure is quite different from **11** as C−O had been incorporated into the borole ring, rather than C−N. Moreover, the product exists as a dimer in the solid state rather than the monomer in **11**.

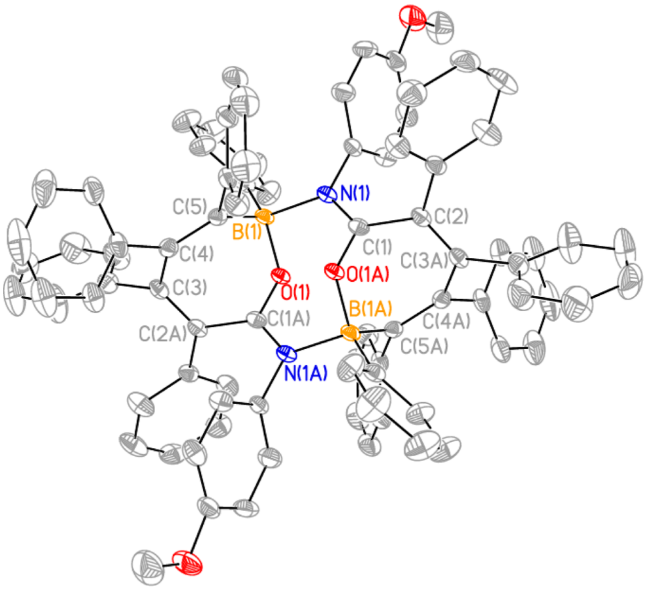


Figure 4. Solid-state structure of **12′**. Hydrogen atoms were omitted for clarity. Compound **12′** crystallizes with two independent molecules in the asymmetric unit; only one molecule is shown and discussed. However, the metrical parameters are similar for both molecules. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): B(1)−O(1) 1.540(3), B(1)−N(1) 1.640(3), N(1)−C(1) 1.301(3), C(1)−O(1A) 1.307(3).

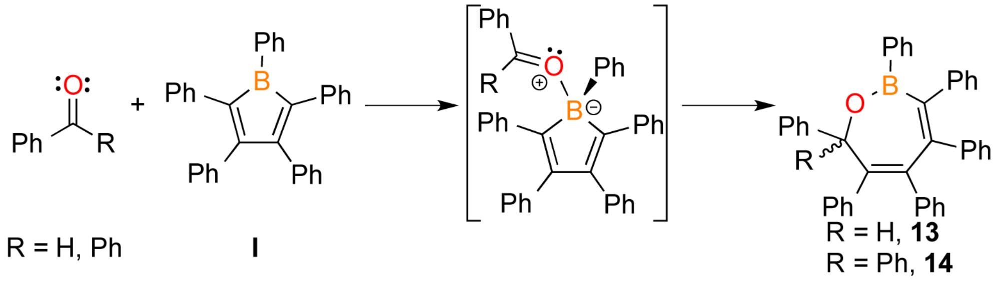
The mechanism likely occurs in a similar fashion. The isocyanate coordinates to the boron center of the borole, followed by ring expansion to the electrophilic carbon atom, formally resulting in a 1,2-insertion into the borole ring. However, in this case, the isocyanate prefers coordination through the more nucleophilic oxygen instead of the nitrogen atom.[80] This is clearly governed by an electronic effect as adamantyl is significantly bulkier than a *para*-methoxyphenyl group. Without a bulky group adjacent to the boron atom, the system undergoes dimerization in the solid state via coordination of the exocyclic imidate nitrogen atom to the boron center of another monomer. The C−N and C−O bond distances from the central carbon of the isocyanate are 1.301(3) Å and 1.307(3) Å, respectively, indicating delocalization in the imidate unit. In solution, there is evidence that only monomer (**12**) is present based on a single resonance in the $^{11}B\{^1H\}$ NMR spectrum at 48 ppm, consistent with a three-coordinate boron center. Compound **12** is unstable in solution at room temperature for extended periods of time.[81]

From the results with isocyanates reacting as a 1,2-dipole, we envisioned that a simple ketone or aldehyde would readily react with the borole to produce new seven-membered heterocycles (Scheme 2). The addition of CH_2Cl_2 solutions of benzophenone and benzaldehyde to 1 equiv of borole in the same solvent resulted in the rapid disappearance of the initial blue color to a colorless solution. Removing the volatiles in vacuo, redissolving the solids in $CDCl_3$, and obtaining crude ^1H and $^{11}B\{^1H\}$ NMR spectra suggested new boron species were generated in very high yields (~95%). The resonances in the $^{11}B\{^1H\}$ NMR spectra were both consistent with three-coordinate boron centers (δ = 35 ppm for benzaldehyde and δ = 45 ppm for benzophenone).

Crystals of both products for X-ray diffraction studies were obtained from a diethyl ether solution via vapor diffusion into hexanes. The structures revealed that both formed the expected seven-membered BOC_5 heterocycles (Figure 5, benzaldehyde, **13**; benzophenone, **14**). Both **13** and **14** are in boat-like conformations similar to that of **11**. For **13**, both C1 and C4/C5 rise out of the plane defined by B1−O1−C2−C3; the angles between this plane and those defined by O1/C1/C2 and B1/C3/C4/C5 (θ_{prow} and θ_{stern}, see Figure 5c) are 40.7(2)° and 59.6(2)°, respectively. It is noteworthy that the phenyl group on the sp^3-hybridized carbon (formerly from the carbonyl carbon) sits in a equatorial position, leaving the hydrogen atom occupying the axial site on the prow of the boat as expected for the lowest energy conformation (Figure 5b). The molecule crystallizes in the $P\bar{1}$ space group with two molecules of the *R*-enantiomer in the asymmetric unit. Because of the inherent center of symmetry in the $P\bar{1}$ space group, the *S*-enantiomer is also present in a 1:1 ratio. The six phenyl substituents are arranged in a propeller-like arrangement outside the seven-membered ring.

The structure of the benzophenone product **14** is overall very similar to that of the benzaldehyde product **13**, with the exception that a second phenyl group occupies the axial site of the quaternary carbon (C1, Figure 5f). In the boat-like seven-membered boracycle, both C1 and C4/C5 rise out of the plane defined by B1−O1−C2−C3; the angles between this plane and those defined by O1−C1−C2 and B1−C3−C4−C5 (θ_{prow} and

Scheme 2. Reaction of Borole I with Benzaldehyde or Benzophenone to Produce 13 or 14, Respectively



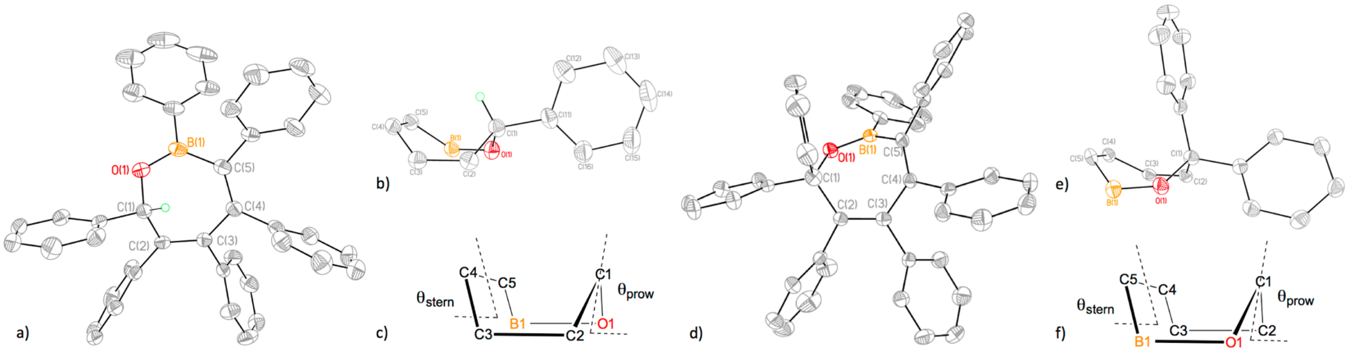


Figure 5. (a) Solid-state structure of **13**. Hydrogen atoms except on the chiral carbon center were omitted for clarity. Ellipsoids are drawn at the 50% probability level. Compound **13** crystallizes with two independent molecules in the asymmetric unit; only one molecule is shown and discussed. However, the metrical parameters are similar for both molecules. Selected bond lengths (Å): B(1)−O(1) 1.364(4), O(1)−C(1) 1.449(4), C(1)−C(2) 1.514(4), C(2)−C(3) 1.356(5), C(3)−C(4) 1.492(4), C(4)−C(5) 1.359(5), C(5)−B(1) 1.582(5); (b) View of the seven-membered ring; (c) Diagram illustrating the dihedral planes ϑ_{prow} and ϑ_{stern} defining the deviation of the ring from planarity into a boat-like conformation; (d) Solid-state structure of **14**. Hydrogen atoms were omitted for clarity. Ellipsoids were drawn at the 50% probability level. B(1)−O(1) 1.354(4), O(1)−C(1) 1.453(3), C(1)−C(2) 1.545(4), C(2)−C(3) 1.352(4), C(3)−C(4) 1.488(4), C(4)−C(5) 1.360(4), C(5)−B(1) 1.560(4). (e) View of the seven-membered ring in **14**. (f) Diagram illustrating the dihedral planes ϑ_{prow} and ϑ_{stern} defining the deviation of the ring from planarity into a boat-like conformation.

θ_{stern}) are 38.4(2)° and 48.5(1)°, respectively, which are slightly smaller at 40.7(2)° and 59.6(2)° for compound **13**. Interestingly, only two other BOC_5 heterocycles have been structurally characterized, both of which are fully saturated.[82−84]

■ CONCLUSIONS

Through these studies, a new series of seven-membered boron heterocycles was synthesized via high-yielding ring-expansion reactions of pentaphenylborole with 1,2-dipolar molecules. The nucleophilic site of the isocyanate proved to be influential on the reaction outcome by inserting either a C−N or a C−O moiety into the ring. This indicates that the system is tunable based on the substrate. These species represent the first crystallographically characterized BNC_5 and BOC_5 heterocycles with unsaturation around the boron center. This ring-expansion method should be practical with other dipolar molecules to generate novel boracycles and opens new vistas in heterocycle chemistry.

■ EXPERIMENTAL SECTION

General. All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Unilab glovebox or using standard Schlenk techniques. Solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over molecular sieves. 4-Methoxyphenyl isocyanate was purchased from Alfa Aesar and used as received. 1-Adamantyl isocyanate and benzophenone were purchased from Acros Organics and used as received. Benzaldehyde was purified by distillation prior to use. Borole **I** was prepared via the literature procedure.[11] Solvents for NMR spectroscopy ($CDCl_3$) were purchased from Cambridge Isotope Laboratories and dried by stirring for 3 d over CaH_2, distilled prior to use and stored over 4 Å molecular sieves. Multinuclear NMR spectra were recorded on Varian VNMRS 500 MHz, Bruker 360 or 600 MHz spectrometers. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on the solid samples. Single-crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo Kα radiation (λ = 0.710 73 Å). Crystals were selected under paratone oil, mounted on micromounts, and then immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL.[85] For compound **11**, the toluene solvate was found to be disordered to an extent that could not be modeled, and the contribution of the toluenes (1.5 in the asymmetric unit) was removed from the reflection data using the squeeze function in the PLATON software suite.[86]

Synthesis of **11**: At room temperature, a solution of 1-adamantyl isocyanate (11.8 mg, 0.067 mmol) in toluene (0.5 mL) was added to a solution of borole **I** (30.0 mg, 0.067 mmol) in toluene (1 mL). The color changed from dark blue to colorless immediately following the addition. After 5 min, the solvent was removed in vacuo giving a white solid. The solids were washed with hexanes (2 × 0.3 mL) and dried in vacuo to give **11** as a white powder. Yield: 33.8 mg, 81%; single crystals for X-ray diffraction studies were grown from a diethyl ether solution of **11** by vapor diffusion into hexanes. dec = 107 °C (turns dark red); ^1H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 7.5 Hz, 2H, C_6H_5), 7.70−7.67 (m, 1H, C_6H_5), 7.62−7.48 (m, 2H, C_6H_5), 7.27 (d, J = 7.5, 2H, C_6H_5), 7.22−7.17 (m, 3H, C_6H_5), 7.12 (d, J = 7.5 Hz, 2H, C_6H_5), 7.05−6.87 (m, 6H, C_6H_5), 6.86−6.68 (m, 6H, C_6H_5), 2.14−1.75 (m, 9H, Ad), 1.56−1.27 (m, 6H, Ad); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.0, 150.8, 144.3, 140.7, 139.6, 138.8, 138.5, 137.9, 137.5, 137.0, 136.9, 134.4, 131.5, 130.9, 130.5, 130.4, 130.4, 128.3, 128.3, 127.7, 127.3, 127.2,126.9, 126.7, 126.7, 57.3, 41.0, 36.3, 29.6; Despite numerous attempts a $^{11}B\{^1H\}$ NMR signal was not observed; FT-IR (cm^{-1}(ranked intensity)): 2907(4), 2247(10), 1642(6), 1594(12), 1488(7), 1437(9), 1262(2), 1152(15), 1075(11), 866(13), 733(3), 694(1), 585(8), 543(5), 518(14). High-resolution mass spectrometry (HRMS) electrospray ionization (ESI): calcd. for $C_{45}H_{41}BNO$ $[M + H]^+$: 622.3203; found 622.3165.

Synthesis of **12**: At room temperature, a solution of 4-methoxyphenyl isocyanate (10.0 mg, 0.067 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of borole **I** (30.0 mg, 0.067 mmol) in CH_2Cl_2 (1 mL). The color changed from dark blue to colorless immediately following the addition. After 5 min, the solvent was removed in vacuo to produce a white solid. The solids were washed with hexanes (2 × 0.3 mL) and dried in vacuo to give a white powder. Yield: 32.8 mg, 82%; dec = 102 °C (turns dark red); single crystals for X-ray diffraction studies were grown from a diethyl ether solution of **12′**. A dimerized form of **12** for X-ray diffraction studies was grown from a diethyl ether solution of **12** by vapor diffusion into hexanes. ^1H NMR (600 MHz, $CDCl_3$) δ 7.40−7.38 (m, 2H, C_6H_5), 7.25−7.23 (m, 1H, C_6H_5), 7.17−7.13 (m, 4H, C_6H_5), 7.11−6.84 (m, 18H, C_6H_5), 6.72 (d, J = 8.4 Hz, 2H, p−MeO-C_6H_4), 6.65 (d, J = 8.4 Hz, 2H, p−MeO-C_6H_4), 3.69 (s, 3H, p−CH_3O-Ph); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 178.3, 158.2, 148.3, 142.1, 139.7, 139.0, 137.8, 137.6, 135.8, 135.3, 133.8, 130.7, 130.6, 130.4, 129.5, 129.3, 128.0, 127.8, 127.6, 127.5, 127.3, 127.1, 126.9, 126.3, 114.2, 55.4; $^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ = 48 (br). FT-IR (cm^{-1}(ranked intensity)): 3051(10), 1596(8), 1507(3), 1487(13), 1440(6), 1243(2), 1208(5), 1168(11), 1070(12), 913(15), 829(7), 730(9), 694 (1), 578(14), 529(4).

Synthesis of **13**: At room temperature a solution of benzaldehyde (7.2 mg, 0.068 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of borole **I** (30.0 mg, 0.067 mmol) in CH_2Cl_2 (1 mL). The color changed from dark blue to colorless immediately following the addition. After 20 min, the solvent was removed in vacuo to produce a white solid. The solids were washed with pentane (3 × 1 mL) and dried in vacuo to give a white powder. Yield: 34.7 mg, 91%; mp = 148−149 °C; single crystals for X-ray diffraction studies were grown from a diethyl ether solution of **13** by vapor diffusion into hexanes. ^{1}H NMR (360 MHz, $CDCl_3$) δ = 7.80−7.71 (m, 2H, C_6H_5), 7.43 (dd, J = 7.6, 5.2 Hz, 3H, C_6H_5), 7.38−7.29 (m, 2H, C_6H_5), 7.26−7.00 (m, 11H, C_6H_5), 6.98−6.89 (m, 2H, C_6H_5), 6.86−6.71 (m, 10H, C_6H_5), 5.16 (s, 1H, CH); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 151.3, 143.7, 140.8, 140.7, 140.1, 138.9, 137.2, 135.2, 135.1, 132.2, 132.1, 131.4, 130.8, 129.7, 128.6, 128.4, 127.8, 127.4, 127.1, 127.0, 126.9, 126.6, 126.3, 125.8, 125.7, 125.1, 77.4; $^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ = 35 (br); FT-IR (cm^{-1}(ranked intensity)): 3054(15), 2962(9), 1597(8), 1488(6), 1437(7), 1327(13), 1259(3), 1071(12), 1010(2), 796(4), 737(11), 696(1), 587(14), 568(10), 542(5).

Synthesis of **14**: At room temperature, a solution of benzophenone (12.3 mg, 0.067 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of borole **I** (30 mg, 0.067 mmol) in 1 mL of CH_2Cl_2. The color changed from dark blue to colorless immediately following the addition. After 30 min, the solvent was removed in vacuo to produce a white solid. The solids were washed with hexane (3 × 1 mL) and dried in vacuo to give **14** as a white powder. Yield: 37.2 mg, 86%; mp = 205−207 °C; single crystals for X-ray diffraction studies were grown from a diethyl ether solution of **14** by vapor diffusion into hexanes. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23−8.21 (m, 1H), 8.03−7.89 (m, 2H), 7.79−7.70 (m, 1H), 7.55 (td, J = 7.4, 1.7 Hz, 1H), 7.51−7.36 (m, 5H), 7.10−6.85 (m, 12H), 6.85−6.75 (m, 3H), 6.75−6.61 (m, 3H), 6.61−6.53 (m, 2H), 6.27−6.16 (m, 2H);$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ = 151.9, 148.0, 147.4, 146.9, 146.3, 146.2, 144.3, 141.7, 140.9, 140.8, 140.7, 139.6, 138.4, 135.6, 131.5, 131.0, 130.9, 130.8, 130.7, 130.2, 129.4, 128.7, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 127.2, 127.1, 127.0, 126.8, 126.7, 126.5, 126.3, 126.2, 126.1, 126.0, 125.5, 125.4, 125.2, 87.2; $^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ = 45 (br); FT-IR(cm^{-1}(ranked intensity)): 3054(9), 1597(6), 1489(3), 1441(5), 1304(15), 1265(2), 1185(12), 1072(10), 1026(7), 759(11), 737(8), 695(1), 636(14), 569(13), 543(4).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray data, IR and NMR spectra, structure of **15**, decomposition of **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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(78) The two known 1,2-BNC$_5$ heterocycles were prepared by the reaction of 9-borabicyclononyl chloride (9-BBN-Cl) with trimethylsilyl azide and the induced rearrangement of an ammonia adduct of a cyclic borane. The other related example is a 1,4-BNC$_5$ heterocycle formed via the cyclization of BH(C$_6$F$_5$)$_2$ with *N,N*-diisopropylallylamine.

(79) Compound **11** decomposed to a mixture of products, see Supporting Information for experimental data.

(80) We base this rationale on the resonance contributors and inductive effects of the *para*-methoxyphenyl and adamantyl groups.

(81) After stirring a CDCl$_3$ solution of **12** for 24 h at room temperature, a new boron species was observed by ^{11}B{^{1}H} NMR (δ = 30), which was identified as 2,4,6-triphenylboroxin (BOPh)$_3$ by X-ray diffraction studies (see Supporting Information for ^{11}B{^{1}H} NMR monitoring). The ^{1}H NMR spectrum revealed a complex mixture. Complete decomposition was observed after 48 h.

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