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Coordination and Ring Expansion of 1,2-Dipolar Molecules with 9-Phenyl-9-borafluorene

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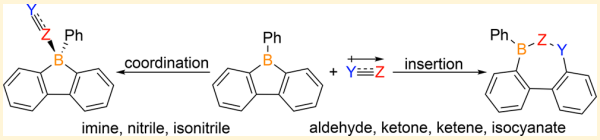
Supporting Information

ABSTRACT: The reactivity of 9-phenyl-9-borafluorene with a series of 1,2-dipolar organic molecules is investigated, revealing that either adducts or seven-membered heterocycles are generated. A nitrile, imine, and isonitrile formed the corresponding coordination complexes that showed no evidence of conversion to ring expanded products. An aldehyde, ketone, and ketene inserted the C═O moiety into the endocyclic B−C bond resulting in BOC_5 boracycles. Isocyanates inserted either C═N or C═O depending on the polarization of the substrate with the former being the only substrate to generate a BNC_5 ring system. The results demonstrate the potential of 9-borafluorenes as effective reagents to generate seven-membered boracycles with a biphenyl backbone.



INTRODUCTION

9-Borafluorenes (**1**) are boron-containing analogues of the ubiquitous polycyclic aromatic hydrocarbon, fluorene.[1] The presence of the tricoordinate boron atom permits conjugation with the benzo-fused rings, which has led to these compounds being explored as electron-transporting materials and sensors and used in optoelectronic devices.[2] Although 9-borafluorenes have been known since 1963,[3] research devoted to these species has recently increased due to the emergence of the aforementioned applications. An appealing feature of 9-borafluorenes is the opportunity for structural diversity by varying substitution on boron as well as on the biphenyl backbone. This presents the ability to tune the electrochemical potential, Lewis acidity, photophysical properties, and stability.[2d,g−i,4] The stability can be significantly increased by installing a sterically encumbering substituent on the boron center, even to the extent of making the 9-borafluorene air stable.[2a,4i,o,5] Although the stability is commented on and eluded to in several publications, a void in the literature is the presence of studies documenting which functionalities are susceptible to reaction with 9-borafluorenes. To advance the chemistry of 9-borafluorenes, understanding the reactivity of these species is imperative.

In regard to reactivity, the endocyclic B−C bond is the most susceptible to cleavage. The first report of B−C bond cleavage was by Köster[3] upon reaction with hydride sources which was later elaborated in further work by Wagner.[6] Bettinger was the first to report that 9-borafluorenes are able to insert atoms in the ring to generate unsaturated boracycles. This was accomplished by utilizing 9-borafluorenes with specific substitution on boron that promoted an intramolecular ring insertion incorporating nitrogen into the core of the borafluorene. Specifically, an NH(OTMS) group on boron [**1NH(OTMS)**] generated 9,10-B,N-phenanthrene[4p,7] **A**, and the B-azido substituted 9-borafluorene $\mathbf{1N_3}$ resulted in the expulsion of N_2 to furnish the corresponding B,N-phenanthryne **B** that could be trapped or ultimately underwent tetramerization (Scheme 1).[7b,8] Wagner demonstrated that reduction of the dimeric 9-H-9-borafluorene ($\mathbf{1H_2}$) resulted in dehydrogenation and formation of six-membered B_2C_4 rings with the two boron atoms in the bridging positions (**C**).[9] Wagner, Wang, and coworkers[10] studied the photolysis of tetra-coordinate anionic 9-borafluorenes **1Mes(Ar)** that resulted in selective insertion of the α-carbon of one of the aryl groups to form boratanorcaradienes (**D**).

Recently, Fukushima and co-workers reported an intermolecular insertion protocol to dibenzoborepin species via the insertion of aryl- or alkyl-substituted alkynes into the B−C bond of 9-chloro-9-borafluorene (**E**, Scheme 2).[11] The scope was broad for alkyl- and aryl-substituted alkynes, but bis(trimethylsilyl)acetylene reacted in a 2:1 fashion to give a 7-membered ring with an exocyclic allene (**F**). This year, our group, and subsequently He, described the intermolecular reaction of 9-borafluorenes with organic azides generating 9,10-B,N-phenanthrenes (**G** and **H**) by insertion of the α- or γ-nitrogen into the B−C bond.[12]

With respect to 1,2-dipolar substrates, the only report of an insertion is the reaction of 1-adamantylphosphaalkyne into 9-phenyl-9-borafluorene (**1Ph**) to furnish the 1,3-phosphaborepin **I** (Scheme 3).[13] Provided that 1-adamantylphosphaalkyne inserted into 9-borafluorenes, we postulated that reactions with 1,2-dipolar substrates may be an efficient means to access unsaturated seven-membered rings. Although limited studies have been reported on intermolecular insertion reactivity for 9-boraflourenes, the chemistry is somewhat reminiscent of their

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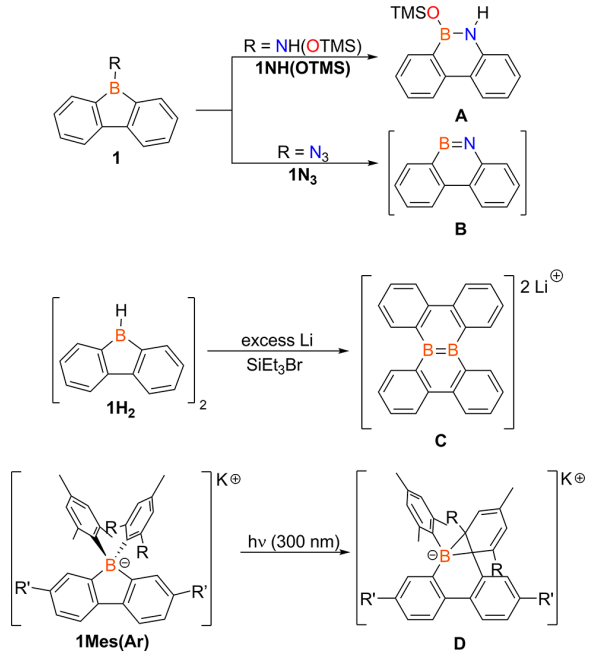
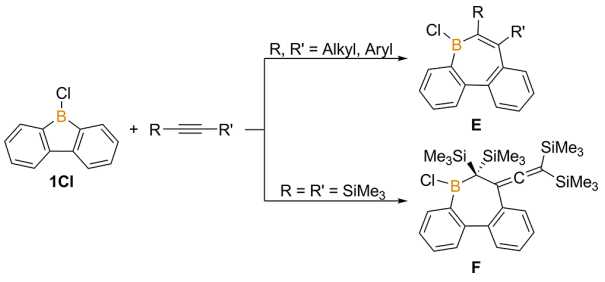
Scheme 1. Intramolecular Insertion Reactions of N- and H-Substituted 9-Borafluorenes[a]



[a]R = H, R′ = H; R = H, R′ = tBu; R = CH_3, R′ = H; R = CH_3, R′ = tBu.

Scheme 2. Insertion Reactions of Alkynes into 9-Chloro-9-borafluorene (1Cl)

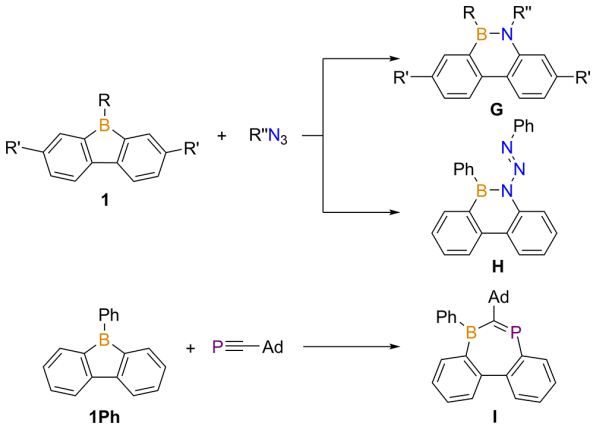


nonaryl-fused relatives, boroles, which readily inserted a variety substrates, including 1,2- and 1,3-dipolar molecules, to generate a wealth of seven and eight-membered rings.[14] In this context, we herein report a reactivity study of **1Ph** with a series of 1,2-dipolar organic molecules.

RESULTS AND DISCUSSION

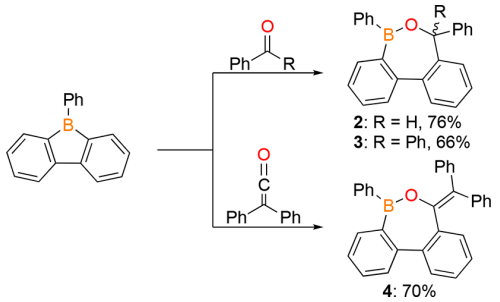
A stoichiometric amount of benzaldehyde was added to a $CDCl_3$ solution of **1Ph** at room temperature (Scheme 4). The singlet for the C_α proton of benzaldehyde enabled monitoring of the reaction by ^1H NMR spectroscopy revealing the emergence of product with a significant upfield shift (δ = 6.12 cf. benzaldehyde δ = 10.01, Figure 1), which converged to a single product after 48 h. Acquiring a $^{11}B\{^1H\}$ NMR spectrum of the product revealed an upfield shift from **1Ph** (45.3 ppm vs **1Ph** 64.0 ppm). An X-ray diffraction study on crystals grown identified the compound as the BOC_5 heterocycle **2** with the C═O unit inserted into one of the endocyclic B−C bonds (Figure 2, Table 1). The compound crystallized with two

Scheme 3. Insertion Reactions of Polar Molecules into 9-Borafluorenes[a]



[a]Ad = 1-adamantyl, Mes = 2,4,6-trimethylphenyl. Substitution for the products generated: **G**, R = Ph, R′ = H, R″ = Ad; R = Ph, R′ = H, R″ = Mes; R = Ph, R′ = Br, R″ = Mes; R = Cl, R′ = H, R″ = Ad; R = Cl, R′ = H, R″ = Ph; **H**, R = R″ = Ph, R′ = H.

Scheme 4. Carbon−oxygen Insertion Reactions of 1Ph with Benzaldehyde, Benzophenone, and Diphenylketene[a]



[a]Reaction conditions: **2**: rt, CH_2Cl_2, 48 h; **3**: 100 °C, toluene, 10 d; **4**: 100 °C, toluene, 7 d.

molecules in the asymmetric unit representing each of the *R* and *S*-enantiomers with the chiral center derived from the *α*-carbon of benzaldehyde. Scaling up the reaction in CH_2Cl_2 and following work up, **2** was isolated as a white powder in 76% yield.

The corresponding reaction with benzophenone in toluene was monitored by $^{11}B\{^1H\}$ NMR spectroscopy (Figure S-7). At room temperature, no change was observed. However, heating the reaction to 100 °C for 10 days led to the convergence to a single resonance in the tricoordinate region at 45.5 ppm. X-ray diffraction studies identified the complex as the C═O insertion product **3**, which following workup, was obtained as a white solid in 66% yield.

Diphenylketene presents additional complexity as it bears an olefin adjacent to the carbon−oxygen double bond. A toluene solution of diphenylketene was added to **1Ph**, and no change was detected at room temperature by $^{11}B\{^1H\}$ NMR spectroscopy. Heating at 100 °C for 7 days resulted in the convergence to a single peak at 45.5 ppm, reminiscent of **2** and **3** (**2**: 45.3 ppm, **3**: 45.5 ppm). The aforementioned shift and obtaining a solid-state structure confirmed the product as the BOC_5 heterocycle akin to the benzaldehyde and benzophe-

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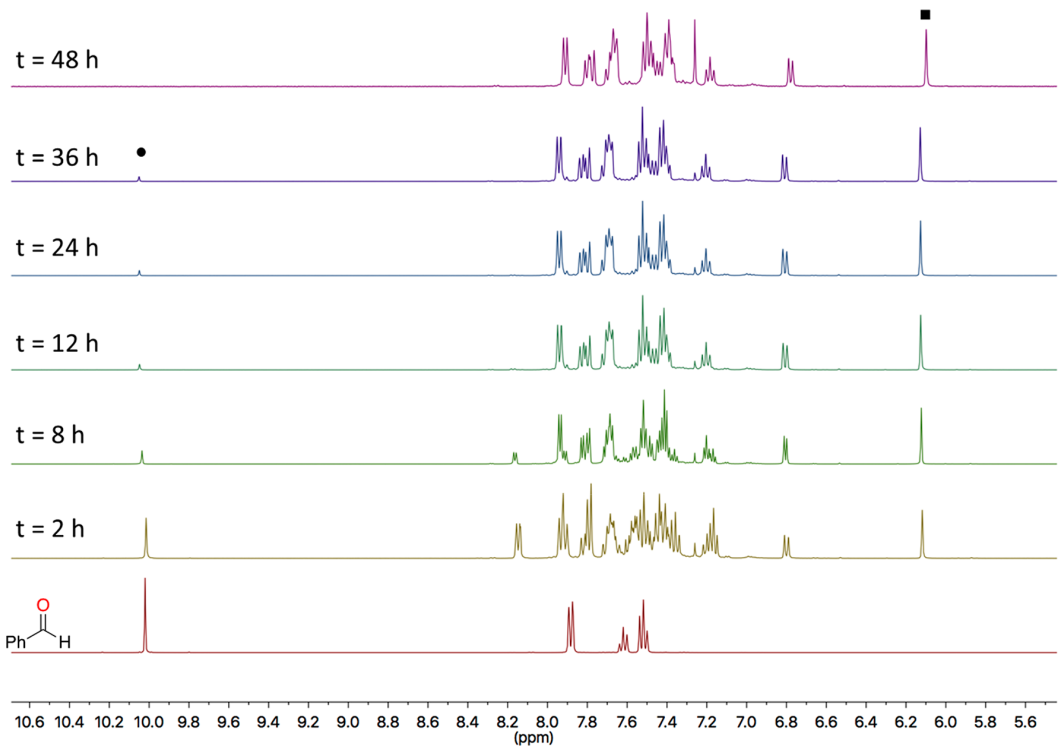

Figure 1. In situ ^{1}H NMR stack plot of the reaction of **1Ph** with benzaldehyde. ● = C_{α} proton of benzaldehyde (10.01 ppm), ■ = C_{α} proton of **2** (6.12 ppm).

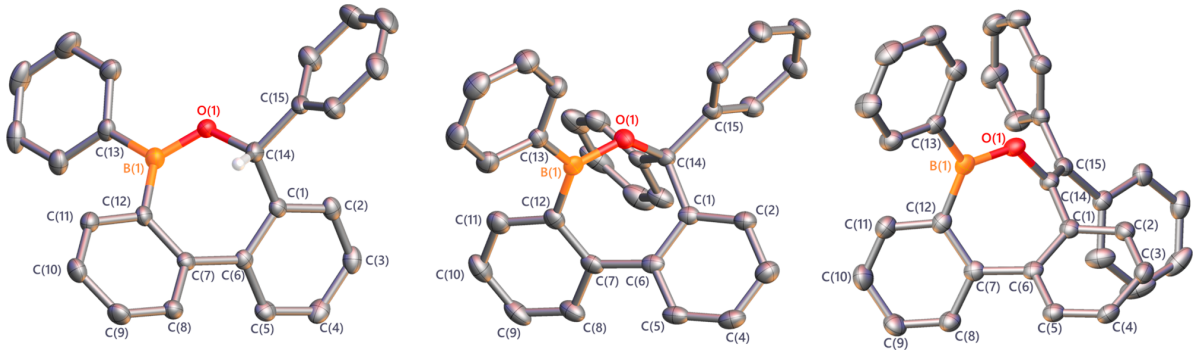

Figure 2. Solid-state structures of **2**–**4** (left to right). Hydrogen atoms are omitted for clarity (except the proton on the sp^3 carbon), and ellipsoids are drawn at the 50% probability level. Compound **2** crystallizes with two independent molecules in the asymmetric unit, and one molecule is shown and discussed as the metrical parameters are comparable for both molecules. Metrical parameters common to the three structures are listed in Table 1. Notable bond length in **4**: C(14)–C(15) 1.339(2) Å.

none C═O insertion reactions, with the exception of an exocyclic C═C double bond.

The aforementioned C═O chemistry to access BOC_5 heterocycles clearly demonstrates the potential of **1Ph** inserting 1,2-dipolar substrates into the endocyclic B–C bond. We turned our attention to unsaturated carbon–nitrogen systems to determine their propensity to form BNC_5 ring systems. The only reported reaction is by Piers and co-workers of acetonitrile with the fully fluorinated version of **1Ph** that formed an adduct, but heating was not attempted to induce seven-membered ring formation.[4h] A CH_2Cl_2 solution of benzylideneaniline was added to a solution of **1Ph** in the same solvent. In situ $^{11}B\{^{1}H\}$ NMR spectroscopy indicated that after 5 min the tricoordinate boron signal from the starting 9-borafluorene (δ = 64.0) disappeared giving rise to a peak at 3.2 ppm, indicative of an sp^3 boron center (Figure S-20). X-ray diffraction studies identified the compound as the aldimine adduct **1Ph·N(Ph)CH(Ph)** with an isomerization of the aldimine from the *E* to the *Z* isomer upon coordination, which has been observed in other aldimines coordinating to boron.[14b,15] After workup, **1Ph·N(Ph)CH(Ph)** was obtained in 94% yield (Scheme 5). Acquiring an ^{1}H NMR spectrum in $CDCl_3$ revealed the diagnostic aldimine proton shifted downfield from 8.45 to 9.11 ppm. Stirring or heating solutions of **1Ph·N(Ph)CH(Ph)** for extended periods of time did not induce further reactivity (100 °C for 14 days).

Exploring the chemistry of **1Ph** with C≡N systems, namely acetonitrile and *tert*-butylisonitrile, **1Ph** was reacted with

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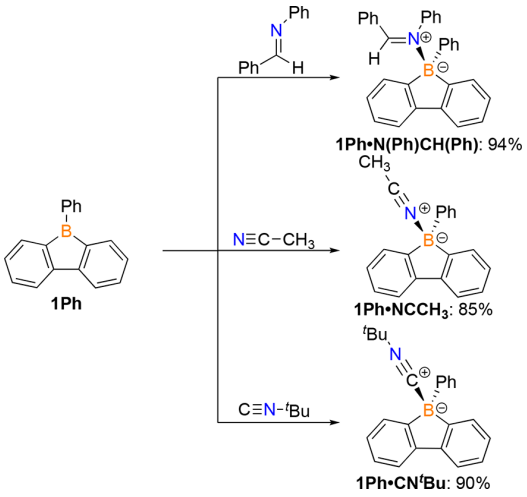
Table 1. Bond Lengths (Å) and Angles (deg) for the BOC_5 Ring System in Heterocycles 2−4

	2	3	4
B(1)−O(1)	1.358(2)	1.366(3)	1.366(2)
O(1)−C(14)	1.444(19)	1.450(2)	1.399(18)
C(14)−C(1)	1.520(2)	1.537(3)	1.487(2)
C(1)−C(6)	1.407(2)	1.415(3)	1.408(2)
C(6)−C(7)	1.494(2)	1.491(3)	1.489(2)
C(7)−C(12)	1.413(2)	1.412(3)	1.413(2)
C(12)−B(1)	1.565(3)	1.564(3)	1.566(2)
B(1)−C(13)	1.557(2)	1.564(3)	1.564(2)
C(14)−C(15)	1.512(2)	1.542(3)	1.339(2)
O(1)−B(1)−C(12)	121.09(15)	121.47(19)	120.76(15)
C(13)−B(1)−O(1)	116.30(16)	113.71(18)	114.92(14)
C(13)−B(1)−C(12)	122.48(16)	124.81(18)	124.30(15)
B(1)−O(1)−C(14)	120.26(13)	124.77(16)	120.76(15)
biphenyl torsion angle	44.6(2)	43.0(2)	43.1(2)

Scheme 5. Reactions of 1Ph with Unsaturated Carbon−Nitrogen Molecules[a]



[a]Reaction conditions are all at room temperature in CH_2Cl_2 with a reaction time of 5 min. The reaction to form **1Ph·NCCH$_3$** is reversible based on $^{11}B\{^1H\}$ NMR spectroscopy.

acetonitrile in a 1:1 ratio at room temperature which converged to a single resonance in the $^{11}B\{^1H\}$ NMR spectrum at 47.7 ppm within 5 min. Growing X-ray diffraction quality crystals identified this compound as the nitrogen-coordinated adduct **1Ph·NCCH$_3$** (Scheme 5). The singlet corresponding to the methyl peak of acetonitrile is shifted slightly downfield to 2.14 ppm from free acetonitrile at 2.10 ppm. The slight downfield shift signifies a weak complex, which is further supported by the acetonitrile adduct of the more Lewis acidic fully fluorinated variant of **1Ph** by Piers and co-workers which has a methyl shift at 2.66 ppm.[4h] Upon workup, compound **1Ph·NCCH$_3$** was obtained in 85% yield. The FT-IR spectrum of the solid featured a diagnostic C≡N stretching mode at 2346 cm^{-1}, consistent with an acetonitrile−borane adduct.[4h,16] Upon heating, no ring-expansion reaction occurred, although variable-temperature $^{11}B\{^1H\}$ NMR spectroscopy indicated a chemical-shift dependence on temperature. At higher temperatures, the resonance is further downfield approaching free borafluorene (Figure S-60), and at lower temperatures the peak shifts upfield in the four-coordinate region, suggesting reversible adduct formation.

The reaction of **1Ph** with *tert*-butylisonitrile was monitored by $^{11}B\{^1H\}$ NMR spectroscopy that indicated the resonance for the tricoordinate boron center disappeared within 5 min giving rise to a new peak at $\delta = -15.1$ indicating quaternization of the boron center (Figure S-33). The identity of the product was determined by X-ray crystallography as the C-coordinated adduct, **1Ph·CN^{t}Bu** (Figure 3, Table 2). The ^1H NMR spectrum showed the singlet corresponding to the *tert*-butyl protons of the isonitrile shifted downfield from 1.44 to 1.55 ppm. The FT-IR spectrum of the solid featured a diagnostic C≡N stretching mode at 2252 cm^{-1} shifted significantly from the free isonitrile (2140 cm^{-1}).[17] Compound **1Ph·CN^{t}Bu** was isolated in 90% yield. Heating the complex gave rise to an indiscernible mixture.

Although BOC_5 seven-membered heterocycles were generated with 1,2 dipolar C═O substrates, namely an aldehyde, ketone, and ketene, carbon−nitrogen 1,2-dipolar substrates formed Lewis acid−base adducts that do not readily convert to BNC_5 seven-membered rings. Prompted by these observations, we were curious about the reactivity of dipolar molecules containing both C═O and C═N, namely, isocyanates. An appealing feature of isocyanates is a second electron withdrawing atom on carbon, enhancing the electrophilicity that may enable the formation of BNC_5 heterocycles.

The reaction of **1Ph** with an equimolar amount of 1-adamantyl isocyanate in CH_2Cl_2 at room temperature was monitored by $^{11}B\{^1H\}$ NMR spectroscopy that indicated the consumption of the starting material ($\delta = 64.0$) and exclusive formation of a single product ($\delta = 50.8$) with a tricoordinate boron center within 5 min (Figure S-40). X-ray diffraction studies identified the compound as the BNC_5 heterocycle **5**, revealing that C−N insertion into the B−C bond of **1Ph** is possible (Figure 4). A C═O stretch at 1696 cm^{-1} in the FT-IR spectrum confirmed the amido group. Following workup, white solids were obtained that were isolated in 97% yield (Scheme 6).

4-Methoxyphenyl isocyanate was reacted with **1Ph** (1:1 ratio) in CH_2Cl_2 at room temperature. In situ $^{11}B\{^1H\}$ spectroscopy NMR showed that the signal corresponding to **1Ph** ($\delta = 64.0$) disappeared, giving rise to a new signal corresponding to a tricoordinate boron center ($\delta = 47.4$). X-ray diffraction studies on crystals grown identified the compound as the BOC_5 complex **6** resulting from the C═O moiety inserting into the ring. The compound crystallizes as the dimer formed by coordination of the nitrogen atom of the exocyclic imidate group to the boron center of a second monomer due to the lack of bulky substituents on boron and nitrogen (Figure 5). It is notable that in solution only the monomeric species was observed by $^{11}B\{^1H\}$ NMR spectroscopy as evidenced by the tricoordinate resonance (Figure S-47). This reaction proved to be high yielding as **6** was isolated in a 93% yield (Scheme 7). The carbon−oxygen insertion observed in the 4-methoxyphenyl isocyanate reaction rather than the carbon−nitrogen insertion of 1-adamantyl isocyanate can be rationalized by the differing polarity of the two isocyanates. In the 1-adamantyl-substituted derivative the nitrogen is the electron-rich center, whereas in 4-methoxyphenyl, the oxygen is the electron-rich center.

The UV−vis absorption data for all compounds have been measured (Figure S-61). The absorbance maxima for all of the reported compounds range between 233 and 238 nm which

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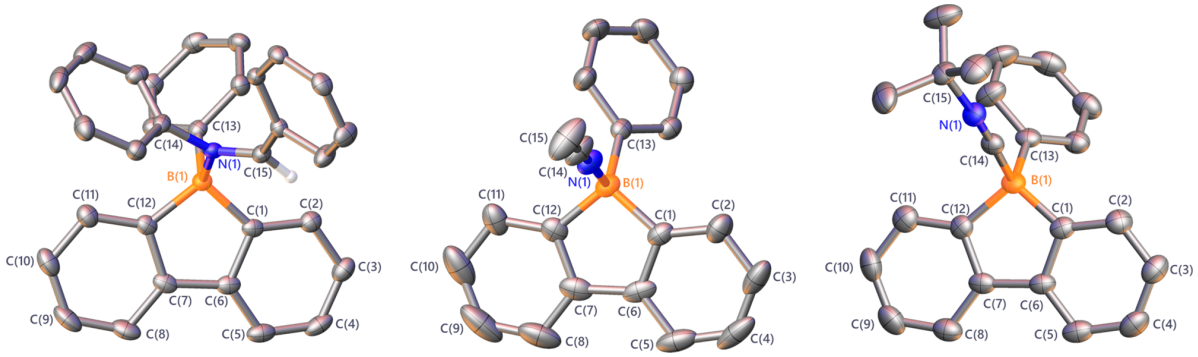


Figure 3. Solid-state structures of **1Ph·N(Ph)CH(Ph)**, **1Ph·NCCH$_3$**, and **1Ph·CN^{t}Bu** (left to right). Hydrogen atoms are omitted for clarity (except the proton on the carbon of the C═N unit of the aldimine), and ellipsoids are drawn at the 50% probability level. For **1Ph·CN^{t}Bu**, only one of the two molecules in the asymmetric unit is shown and representative bond lengths are reported from the molecule depicted. Metrical parameters in the borafluorene core are in listed in Table 2. Other notable bond lengths (Å) and angles (deg): **1Ph·N(Ph)CH(Ph)**, B(1)−N(1) 1.641(2), N(1)−C(15) 1.2883(18); **1Ph·NCCH$_3$**, B(1)−N(1) 1.598(4), N(1)−C(14) 1.128(4), B(1)−N(1)−C(14) 173.3(3); **1Ph·CN^{t}Bu**, B(1)−C(14) 1.608(6), N(1)−C(14) 1.137(4), B(1)−C(14)−N(1) 173.7(4).

Table 2. Bond Lengths (Å) and Angles (deg) of the Borafluorene moiety in 1Ph·N(Ph)CH(Ph), 1Ph·NCCH$_3$, 1Ph·CN^{t}Bu·1Ph

	1Ph·N(Ph)CH(Ph)	1Ph·NCCH$_3$	1Ph·CN^{t}Bu	1Ph[4j]
B(1)−C(1)	1.622(2)	1.620(4)	1.635(6)	1.580(10)
C(1)−C(6)	1.415(2)	1.405(4)	1.400(6)	1.430(10)
C(6)−C(7)	1.479(2)	1.484(5)	1.477(6)	1.512(11)
C(7)−C(12)	1.413(2)	1.406(4)	1.411(5)	1.430(9)
C(12)−B(1)	1.622(2)	1.625(4)	1.610(6)	1.592(10)
B(1)−C(13)	1.6192(2)	1.601(4)	1.620(7)	1.572(9)
C(12)−B(1)−C(1)	99.95(13)	99.8(2)	99.8(3)	104.2(6)
B(1)−C(1)−C(6)	109.02(13)	109.3(3)	108.9(3)	108.1(6)
C(1)−C(6)−C(7)	110.97(14)	110.9(2)	110.8(3)	109.7(6)
C(6)−C(7)−C(12)	110.75(14)	110.7(3)	111.1(3)	110.8(6)
C(7)−C(12)−B(1)	109.31(13)	109.2(3)	108.9(3)	107.1(6)

are very similar to those of **1Ph** (λ_{max} = 241 nm) and other related 9-borafluorenes.[2a,4d,l,o] The adducts **1Ph·NCCH$_3$** and **1Ph·CN^{t}Bu** display a second intense peak at 268 and 281 nm, respectively, as well as a third peak at 317 nm for both. The fluorescence spectra of the compounds with detectable emissions have peaks in the 344−371 nm range (Figure S-62).[18]

The solid-state structures of the BOC$_5$ heterocycles **2**−**4** are all nonplanar seven-membered rings that adopt boat conformations (Figure S-63−68). The biphenyl moiety twists with interplanar angles ranging from 43.0(2)° to 44.6(2)° to accommodate the boat structure. The boron−oxygen bond lengths are all similar [**2**: 1.358(2) Å, **3**: 1.366(3) Å, **4**: 1.366(2) Å] and comparable to known oxoboranes indicating delocalization of the electron density on oxygen to boron.[14a,s,19] Compound **4** has an exocyclic C(1)−C(15) bond length of 1.339(2) Å that confirms the double bond from the ketene is retained in the product. The BNC$_5$ ring in **5** also adopts a boat conformation with a slightly smaller contortion in the diphenyl backbone of 37.5(2)°. The endocyclic B−N bond [1.417(4) Å] is shorter than a typical B−N single bond indicating delocalization of the pi-electron density on nitrogen

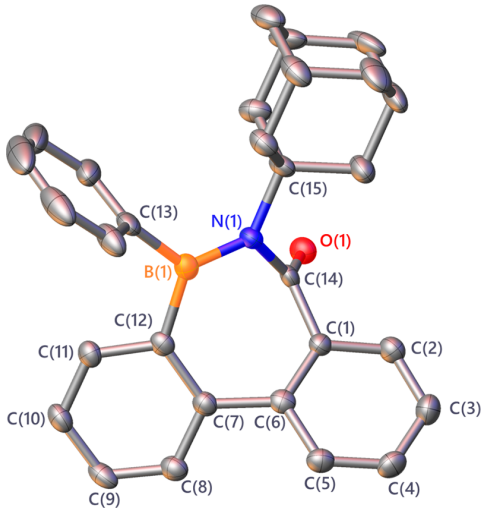
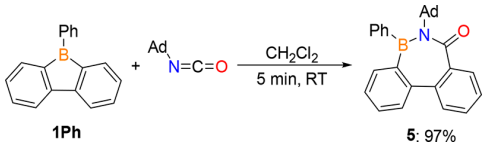


Figure 4. Solid-state structure of **5**. Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): B(1)−N(1) 1.417(4), N(1)−C(14) 1.445(3), C(14)−O(1) 1.209(3), C(14)−C(1) 1.485(4), C(1)−C(6) 1.395(4), C(6)−C(7) 1.483(4), C(7)−C(12) 1.415(4), C(12)−B(1) 1.586(4), B(1)−C(13) 1.579(4), C(12)−B(1)−C(13) 113.2(2), C(12)−B(1)−N(1) 123.0(2), C(13)−B(1)−N(1) 123.6(2), C(15)−N(1)−C(14) 113.3(2), C(15)−N(1)−B(1) 129.2(2), B(1)−N(1)−C(14) 116.7(2).

Scheme 6. Reaction of 1Ph with 1-adamantyl isocyanate



to the boron center[12a,14b,20] and the short carbon−oxygen bond [1.209(3) Å] is consistent with an amido group.[14a] In the dimeric structure **6**, the short C−N and C−O bond lengths [1.300(3) and 1.307(3), respectively] are consistent with delocalization in the amidate moiety.[14a]

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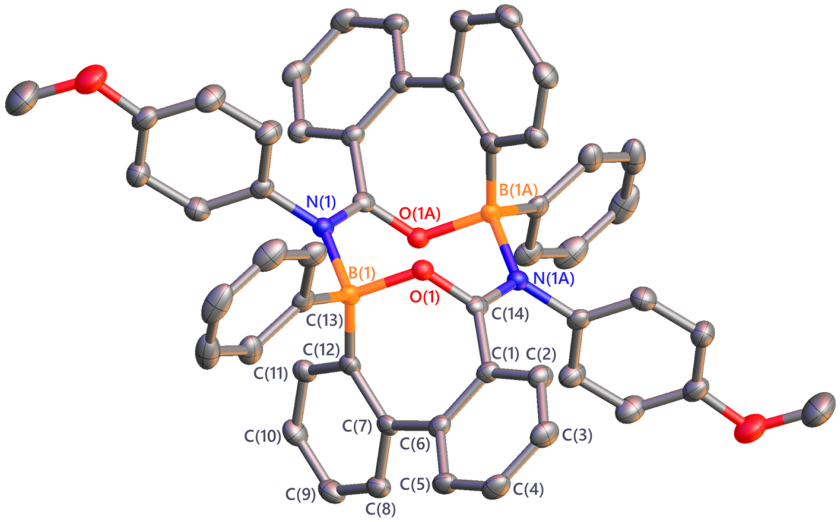
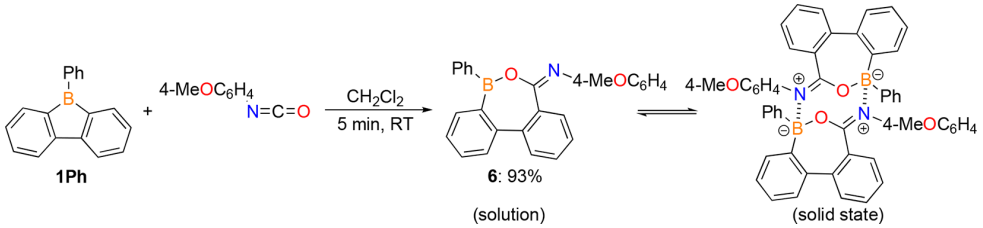


Figure 5. Solid-state structure of **6**. Hydrogen atoms are omitted for clarity and ellipsoids are drawn at the 50% probability level. **6** crystallizes with two independent molecules in the asymmetric unit; for clarity, only one molecule is shown and discussed. The 4-methoxyphenyl group of one molecule in the asymmetric unit exhibits crystallographic disorder (positional) and is therefore not displayed. Selected bond lengths (Å) and angles (deg): B(1)−O(1) 1.528(3), O(1)−C(14) 1.307(3), C(14)−N(1) 1.300(3), C(14)−C(1) 1.488(3), C(1)−C(6) 1.403(3), C(6)−C(7) 1.491(3), C(7)−C(12) 1.418(3), C(12)−B(1) 1.612(3), B(1)−C(13) 1.602(3), C(13)−B(1)−O(1) 109.51(18), C(12)−B(1)−C(13) 113.58(19), C(12)−B(1)−O(1) 113.05(18), B(1)−O(1)−C(14) 120.44(17).

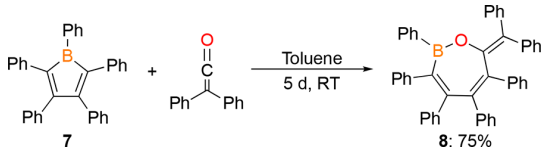
Scheme 7. Reaction of 1Ph with 4-Methoxyphenyl Isocyanate



The Lewis acid−base adducts **1Ph·N(Ph)CH(Ph)**, **1Ph·NCCH$_3$**, and **1Ph·CN^{t}Bu** retain the 9-borafluorene framework and can be compared to the free species. Upon coordination, the B−C bond lengths in the BC$_4$ ring elongate slightly [1.620(4)−1.635(6) Å vs 1.580(10) and 1.592(10) Å][4j] as a consequence of the quaternization of the boron center and change in hybridization from sp^2 to sp^3. The C−C bonds in the boracycle all shorten marginally [C(1)−C(6) 1.400(6)−1.415(2) Å vs 1.430(10) Å; C(6)−C(7) 1.477(6)−1.484(5) Å vs 1.512(11) Å; C(7)−C(12) 1.406(4)−1.413(2) Å vs 1.430(9) Å] presumably due to the disruption of the conjugation and antiaromaticity in the ring.[4j] The carbon−nitrogen multiple bonds of the aldimine, nitrile, and isonitrile are all retained upon coordination [**1Ph·N(Ph)CH(Ph)**: 1.2883(18) Å, **1Ph·NCCH$_3$**: 1.128(4) Å, and **1Ph·CN^{t}Bu**: 1.137(4), respectively].[4h,17]

As mentioned prior, 9-borafluorenes are related to boroles with the difference being the fused aryl groups to the central BC$_4$ ring. It is documented that this feature decreases the antiaromatic character, Lewis acidity, and hence, the reactivity.[4d,f,5,12a] Conveniently, all of the reactions described, with the exception of diphenylketene, have been conducted with pentaphenylborole[14a,b] (**7**), the borole most similar to **1Ph**. The reaction of **7** with diphenylketene proceeded at room temperature going to completion in 5 days as indicated by ^{11}B{^{1}H} NMR spectroscopy converging to a product with a signal at 45.1 ppm (Scheme 8). X-ray diffraction studies confirmed the species to be the C═O insertion product also

Scheme 8. Insertion of Diphenylketene into 7



with an exocyclic C═C double bond (Figure 6). This, and prior results, indicate that benzaldehyde, benzophenone, and diphenylketene react with both **1Ph** and **7** to generate BOC$_5$ heterocycles via C═O insertion. A striking difference is the more sluggish reactions for **1Ph**. In many cases reactions with **1Ph** required heating whereas the borole reactions all proceeded at room temperature (benzaldehyde < 20 min, rt vs 2 d, rt; benzophenone <30 min, rt; vs 10 d, 100 °C, diphenylketene 5 d, rt vs 7 d, 100 °C). The reactions for both isocyantes inserted a C═N or C═O moiety for 1-adamantyl- and 4-methoxyphenyl-substituted isocyanates, respectively, with transformations to both boracycles being completed rapidly (within 5 min).

In the benzylideneaniline reaction, for **7**, the adduct could be observed and crystallized but converted to the BNC$_5$

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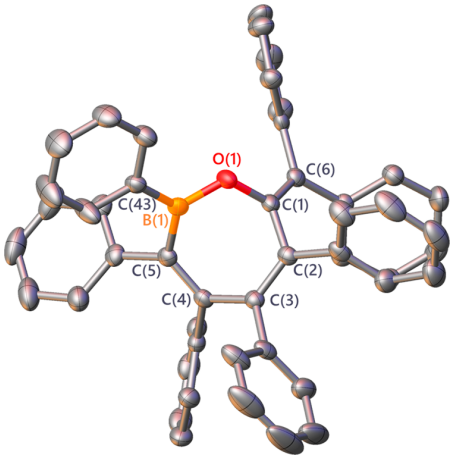

Figure 6. Solid-state structure of **8**. Hydrogen atoms are omitted for clarity and ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) angles (deg): B(1)−O(1) 1.376(3), O(1)−C(1) 1.402(2), C(1)−C(2) 1.489(3), C(2)−C(3) 1.349(3), C(3)−C(4) 1.494(3), C(4)−C(5) 1.353(3), C(5)−B(1) 1.570(3), C(1)−C(6) 1.329(3), B(1)−C(43) 1.553(3), C(43)−B(1)−O(1) 117.00(19), C(43)−B(1)−C(5) 124.01(19), C(5)−B(1)−O(1) 118.95(18), B(1)−O(1)−C(1) 119.58(16).

heterocycle upon stirring at room temperature. The borafluorene reaction generates the adduct but without conversion to the BNC_5 ring system at room temperature or heating to 100 °C. Similarly, acetonitrile forms a weak adduct with **1Ph** that does not undergo insertion, in comparison the isolated borole−acetonitrile adduct converted to the insertion product upon heating to 80 °C for 24 h. Both **1Ph** and **7** readily formed *tert*-butylisonitrile adducts. Heating adduct **1Ph·CN^{t}Bu** produced a complex mixture while heating the isonitrile adduct of **7** led to the isolation of a small amount of an unusual cyano-bridged tetramer. In all cases, the benzofused variant, **1Ph** is less reactive than **7** which is attributed to its lower degree of antiaromaticity. It is notable that no adduct intermediates were observed en route to the seven membered rings for **1Ph** which were observed in the aldimine and nitrile ring expansion reactions with pentaphenylborole.

CONCLUSIONS

The reactions of 9-phenyl-9-borafluorene with 1,2-dipolar molecules are described, revealing that either adducts or seven-membered rings are generated. An aldimine, nitrile, and isonitrile all formed adducts which were resilient or resulted in complex mixtures after heating. Benzophenone, benzaldehyde, diphenylketene, and 4-methoxyphenyl isocyanate inserted a C═O unit into the endocyclic B−C bond to furnish BOC_5 heterocycles whereas 1-adamantyl isocyanate inserted C═N to provide the BNC_5 boracycle. The latter represents the only substrate that yielded a BNC_5 boracycle. It is surprising that this simple insertion reactivity of 9-borafluorenes has not been developed given that these molecules have been known for 55 years. These observations offer insight into a potential methodology to insert atoms into the endocyclic B−C bond of 9-borafluorenes to generate boracycles with extended conjugation.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Unilab glovebox. 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 4 Å molecular sieves (acetonitrile, CH_2Cl_2, toluene, hexanes, *n*-pentane, diethyl ether). **1Ph**,[4f] **7**,[21] diphenylketene,[22] and benzylideneaniline[23] were prepared via the literature procedures. Benzophenone was purchased from Acros Organics and used as received. Benzaldehyde was purchased from Sigma-Aldrich and distilled prior to use. *tert*-Butylisonitrile was purchased from Alfa Aesar and used as received. 1-Adamantyl isocyanate and 4-methoxyphenyl isocyanate were purchased from Sigma-Aldrich and used as received. $CDCl_3$ for NMR spectroscopy was purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH_2, distilled, and stored over 4 Å molecular sieves. Multinuclear NMR spectra were recorded on Bruker 400 or 600 MHz spectrometers. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. High-resolution mass spectra (HRMS) were acquired at the Baylor University Mass Spectrometry Center on a Thermo Scientific LTQ Orbitrap Discovery spectrometer using +ESI. Melting points were measured with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. UV−vis spectra were recorded using an Agilent 8453 UV−vis spectrophotometer. Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer with excitation at the absorbance λ_{max}. Solutions were prepared in a N_2-filled glovebox and measured in screw capped quartz cuvettes for both UV−vis and fluorescence. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo Kα radiation (λ = 0.71073 Å). Crystals were selected under paratone oil, mounted on micromounts, and immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL[24] and figures produced using OLEX2.[25] The purity of all compounds was determined by ^{1}H NMR spectroscopy to be on the order of 95% or higher, and the corresponding spectra are in the Supporting Information.

We have exposed $CDCl_3$ solutions in 5 mm NMR tubes of all of the compounds, in the same concentrations, to ambient conditions for 24 h. Acquiring ^{1}H and ^{11}B{^{1}H} NMR spectra revealed that compounds **2**−**4** do not show any signs of decomposition, while **5** and **6** give rise to a mixture of decomposition products. Adducts **1Ph·N(Ph)CH(Ph)** and **1Ph·NCCH$_3$** decomposed to a new single broad ^{11}B{^{1}H} NMR resonance at ∼47 ppm and a mixture of compounds by ^{1}H NMR spectroscopy. **1Ph·CN^{t}Bu** underwent slight decomposition (∼10%) by both ^{1}H and ^{11}B{^{1}H} NMR spectroscopy with the new boron resonance also at ∼47 ppm. Under a nitrogen atmosphere all compounds have not shown any sign of decomposition over a 3 month period.

Synthesis of 2. At room temperature, benzaldehyde (42.0 μL, 0.417 mmol) was added to a CH_2Cl_2 solution of **1Ph** (100.0 mg, 0.417 mmol; 1 mL). The yellow solution was stirred for 2 d at room temperature resulting in a colorless solution. The volatiles were removed in vacuo to obtain a white residue. The residue was dissolved in *n*-pentane (1 mL) and stored overnight at room temperature to give a white precipitate that was filtered and dried in vacuo to give a white solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of a *n*-pentane solution of **2** into toluene: yield 109.0 mg, 76%; mp 155−158 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, J = 12.0 Hz, 2H), 7.79 (dd, J = 6.0, 18.0 Hz, 2H), 7.73−7.62 (m, 4H), 7.55−7.45 (m, 4H), 7.44−7.35 (m, 4H), 7.21−7.15 (m, 1H), 6.78 (d, J = 12.0 Hz, 1H), 6.10 (s, 1H); ^{13}C{^{1}H } NMR (151 MHz, $CDCl_3$) δ 145.19, 142.34, 141.45, 139.96, 136.80, 136.46, 136.19, 131.30, 130.84, 129.71, 129.28, 128.60, 128.49, 127.79, 127.75, 127.51, 127.30, 127.01, 126.64, 77.31; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 45.3; FT-IR (cm^{-1} (ranked intensity)) 1595 (14), 1437 (7), 1334 (12), 1272 (3), 1246 (13), 975 (11), 918 (6), 762 (5), 743 (2), 728 (10), 694 (1), 649 (4), 603 (9), 576 (15), 509 (8); high-resolution

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mass spectroscopy (HRMS) electrospray ionization (ESI) calcd for $C_{25}H_{20}BO$ $[M + H]^+$ 347.1606, found 347.1606; UV−vis (CH_2Cl_2) λ_{max} (236 nm) ε = 26400 L mol^{-1} cm^{-1}, (390 nm): ε = 2900 L mol^{-1} cm^{-1}.

Synthesis of 3. At room temperature, a solution of benzophenone in toluene (76.0 mg, 0.417 mmol; 1 mL) was added to a solution of **1Ph** (100.0 mg, 0.417 mmol; 1 mL) in toluene. The solution was stirred for 10 d at 100 °C with no observable color change. The volatiles were removed in vacuo to obtain a yellow residue. The residue was dissolved in *n*-pentane (1 mL) and stored overnight at room temperature to give a precipitate that was collected and dried in vacuo to give a white solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of a *n*-pentane solution of **3** into toluene: yield 116.0 mg, 66%; mp 170−173 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 6.0 Hz, 1H), 8.03 (d, J = 6.0 Hz, 2H), 7.65−7.57 (m, 2H), 7.51 (t, J = 6.0 Hz, 1H), 7.47−7.40 (m, 3H), 7.39−7.32 (m, 4H), 7.29 (t, J = 6.0 Hz, 1H), 7.21 (t, J = 6.0 Hz, 1H), 7.19−7.13 (m, 1H), 7.08−7.02 (m, 1H), 6.97−6.92 (m, 1H), 6.88 (t, J = 6.0 Hz, 1H), 6.83 (t, J = 6.0 Hz, 1H), 6.75 (d, J = 12.0 Hz, 1H), 6.72−6.65 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 146.81, 146.40, 145.00, 144.81, 141.70, 136.45, 135.68, 131.62, 131.26, 130.29, 129.92, 129.53, 128.92, 128.72, 128.47, 128.24, 127.86, 127.68, 127.62, 127.32, 127.24, 126.75, 126.62, 126.57, 125.74, 87.01; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 45.5; FT-IR (cm^{-1} (ranked intensity)): 1595 (10), 1489 (14), 1439 (5), 1331 (7), 1265 (4), 989 (6), 947 (12), 910 (9), 766 (8), 740 (3), 697 (1), 647 (2), 592 (11), 535 (13), 503 (15); high-resolution mass spectroscopy (HRMS) electrospray ionization (ESI) calcd for $C_{31}H_{23}BONa$ $[M + Na]^+$ 445.1739, found 445.1731; UV−vis (CH_2Cl_2) λ_{max} (235 nm) ε = 6,700 L mol^{-1} cm^{-1}; fluorescence (CH_2Cl_2) λ_{em} 344 nm.

Synthesis of 4. At room temperature, a toluene solution of diphenylketene (110.0 μL, 0.625 mmol; 1 mL) was added to a solution of **1Ph** (150.0 mg, 0.625 mmol; 1 mL) in toluene. The solution was stirred for 7 d at 100 °C at which point the volatiles were removed in vacuo to obtain a yellow residue. The solid was dissolved in *n*-pentane (1 mL) and stored overnight at room temperature, resulting in the growth of colorless crystals that were suitable for X-ray diffraction studies: yield 190.0 mg, 70%; mp 90−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.63 (m, 3H), 7.60−7.51 (m, 3H), 7.40 (d, J = 8.0 Hz, 2H), 7.38−7.29 (m, 2H), 7.29−7.20 (m, 5H), 7.16 (t, J = 8.0 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 7.04−6.97 (m, 1H), 6.94 (t, J = 4.0 Hz, 3H), 6.77−6.70 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.17, 145.94, 141.42, 140.34, 139.49, 139.05, 137.25, 136.55, 131.49, 131.21, 130.82, 130.57, 128.98, 128.87, 127.93, 127.75, 127.73, 127.44, 127.10, 127.00, 126.55; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 45.6; FT-IR (cm^{-1} (ranked intensity)) 2095 (4), 1594 (6), 1493 (10), 1436 (5), 1275 (2), 1184 (15), 1130 (12), 1028 (11), 910 (9), 739 (3), 694 (1), 647 (8), 603 (7), 511 (14), 481 (13); high-resolution mass spectroscopy (HRMS) electrospray ionization (ESI) calcd for $C_{32}H_{24}BO$ $[M + H]^+$ 435.1920, found 435.1914; UV−vis (CH_2Cl_2) λ_{max} (234 nm) ε = 35200 L mol^{-1} cm^{-1}; fluorescence (CH_2Cl_2) λ_{em} 351 nm.

Synthesis of 1Ph·N(Ph)CH(Ph). At room temperature, a solution of benzylideneaniline (19.0 mg, 0.105 mmol, 1 mL) in CH_2Cl_2 was added to a CH_2Cl_2 solution of **1Ph** (25.0 mg, 0.104 mmol, 1 mL) and stirred for 5 min. The volatiles were removed in vacuo to afford a yellow residue. The solid was washed with *n*-pentane (1 × 1 mL) and dried in vacuo to give **1Ph·N(Ph)CH(Ph)** as a light-yellow powder. Single crystals for X-ray diffraction studies were grown by vapor diffusion of a CH_2Cl_2 solution of **1Ph·N(Ph)CH(Ph)** into toluene: yield 43.0 mg, 94%; mp 183−186 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.66 (d, J = 12.0 Hz, 2H), 7.61 (d, J = 6.0 Hz, 2H), 7.43 (t, J = 6.0 Hz, 1H), 7.33 (d, J = 6.0 Hz, 2H), 7.26−7.16 (m, 10H), 7.08 (t, J = 6.0 Hz, 2H), 6.97 (d, J = 12.0 Hz, 2H), 6.65 (d, J = 12.0 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.80, 160.55, 152.26, 149.46, 145.86, 143.37, 143.25, 136.29, 133.99, 133.37, 132.84, 132.78, 131.94, 131.60, 131.53, 129.85, 129.30, 129.12, 128.96, 128.61, 128.47, 128.31, 127.77, 127.52, 126.97, 126.84, 126.07, 126.01, 124.20, 121.01, 119.37; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 3.2; FT-IR (cm^{-1} (ranked intensity)) 1595 (7), 1490 (11), 1438 (5), 1331 (8), 1267 (3), 1246 (15), 989 (6), 947 (12), 910 (10), 763 (9), 739 (2), 696 (1), 648 (4), 592 (13), 506 (14); high-resolution mass spectroscopy (HRMS) electrospray ionization (ESI) calcd for $C_{31}H_{24}BNNa$ $[M + Na]^+$ 444.1899, found 444.1891.; UV−vis (CH_2Cl_2) λ_{max} (238 nm) ε = 31600 L mol^{-1} cm^{-1}, (316 nm): ε = 12800 L mol^{-1} cm^{-1}; fluorescence (CH_2Cl_2) λ_{em} 371 nm.

Synthesis of 1Ph·NCCH$_3$. At room temperature, acetonitrile (11.0 μL, 0.208 mmol) was added to a CH_2Cl_2 solution of **1Ph** (50.0 mg, 0.208 mmol) and stirred for 5 min. The CH_2Cl_2 solution was purified by vapor diffusion of a CH_2Cl_2 solution of **1Ph·NCCH$_3$** into hexanes and isolated. Subsequent *n*-pentane washes (3 × 1 mL) gave **1Ph·NCCH$_3$** as yellow needles. Single crystals for X-ray diffraction studies were grown by vapor diffusion from a $CHCl_3$ solution of **1Ph·NCCH$_3$** into hexanes: yield 50.0 mg, 85%; mp 114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.88 (m, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 4.0 Hz, 3H), 7.33 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 8.0 Hz, 2H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 151.37, 133.45, 132.37, 130.12, 128.54, 127.95, 127.32, 119.67, 112.75, 2.41; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 47.7; FT-IR (cm^{-1} (ranked intensity)) 3044 (9), 1592 (2), 1470 (15), 1433 (4), 1240 (1), 1182 (13), 1027 (7), 890 (3), 860 (11), 781 (10), 648 (6), 620 (8), 599 (5), 506 (12), 415 (14); high-resolution mass spectroscopy (HRMS) electrospray ionization (+ESI) calcd for $C_{20}H_{17}BN$ $[M + H]^+$ 282.1454, found 282.1451; UV−vis (CH_2Cl_2) λ_{max} (236 nm) ε = 13700 L mol^{-1} cm^{-1}, (268 nm) ε = 11200 L mol^{-1} cm^{-1}, (317 nm): ε = 4000 L mol^{-1} cm^{-1}.

Synthesis of 1Ph·CN^{t}Bu. At room temperature, *tert*-butylisonitrile (94.0 μL, 0.833 mmol) was added to a CH_2Cl_2 solution of **1Ph** (200.0 mg, 0.8330 mmol) and stirred for 5 min. The volatiles were removed in vacuo to give **1Ph·CN^{t}Bu** as an off-white powder. Single crystals for X-ray diffraction studies were grown by vapor diffusion from a $CHCl_3$ solution of **1Ph·CN^{t}Bu** into hexanes: yield 241.0 mg, 90%; dp 124 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 6.0 Hz, 2H), 7.70 (d, J = 6.0 Hz, 2H), 7.50 (d, J = 6.0 Hz, 2H), 7.39 (t, J = 6.0 Hz, 2H), 7.33−7.28 (m, 4H), 7.24 (t, J = 12.0 Hz, 1H), 1.55 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.14, 132.87, 131.47, 128.24, 127.30, 126.90, 126.13, 120.01, 59.64, 30.20; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ −15.1; FT-IR (cm^{-1} (ranked intensity)) 2984 (13), 2252 (3), 1431 (4), 1373 (12), 1236 (15), 1183 (5), 887 (8), 746 (1), 731 (14), 702 (2), 649 (11), 624 (7), 531 (6), 494 (9), 428 (10); high-resolution mass spectroscopy (HRMS) electrospray ionization (+ESI) calcd for $C_{23}H_{23}BN$ $[M + H]^+$ 324.1922, found 324.1920; UV−vis (CH_2Cl_2) λ_{max} (233 nm) ε = 33700 L mol^{-1} cm^{-1}, (281 nm) ε = 8200 L mol^{-1} cm^{-1}, (317 nm) ε = 6200 L mol^{-1} cm^{-1}.

Synthesis of 5. A solution of 1-adamantyl isocyanate (18.0 mg, 0.104 mmol; 1 mL) in CH_2Cl_2 was dropwise added to a solution of **1Ph** (25.0 mg, 0.104 mmol; 1 mL) in CH_2Cl_2 at room temperature. After being stirred for 5 min, a color change was observed from bright yellow to colorless. The solvent was removed in vacuo, and the residue was washed with hexanes (2 × 0.5 mL) to give **5** as a white solid. Single crystals for X-ray diffraction studies were grown by vapor diffusion of a diethyl ether solution of **5** into hexanes: yield 42.0 mg, 97%; mp 151−156 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 6.0 Hz, 2H), 7.60 (d, J = 12.0 Hz, 1H), 7.55 (dd, J = 12.0, 6.0 Hz, 2H), 7.45−7.42 (m, 2H), 7.43−7.38 (m, 2H), 7.37−7.33 (m, 3H), 7.29 (t, J = 6.0 Hz, 1H), 2.19 (s, 6H), 2.02 (s, 3H), 1.58 (s, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 176.41, 141.02, 140.30, 137.40, 136.99, 134.05, 133.60, 130.28, 129.85, 129.50, 128.36, 128.14, 127.77, 127.66, 127.47, 126.68, 61.83, 45.40, 43.05, 42.58, 36.79, 36.25, 35.89, 30.34, 29.92, 29.42; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 50.9 (br); FT-IR (cm^{-1} (ranked intensity)) 2903 (6), 2849 (10), 1696 (13), 1594 (11), 1436 (8), 1304 (7), 1275 (4), 1241 (3), 1091 (12), 1010 (9), 737 (2), 697 (1), 642 (5), 617 (15), 594 (14); high-resolution mass spectrometry (HRMS) electrospray ionization (ESI) calcd for $C_{29}H_{29}BNO$ $[M + H]^+$ 418.2342, found 418.2338; UV−vis (CH_2Cl_2) λ_{max} (236 nm) ε = 4300 L mol^{-1} cm^{-1}.

Synthesis of 6. A solution of 4-methoxyphenyl isocyanate (52.0 μL, 0.417 mmol; 2 mL) in CH_2Cl_2 was added dropwise into a stirring solution of **1Ph** (100.0 mg, 0.417 mmol; 4 mL) in CH_2Cl_2. After the solution was stirred for 5 min, a color change was observed from

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bright yellow to colorless. The solvent was removed in vacuo and the residue was washed with hexanes (2 × 2 mL) to give **6** as a white solid. Single crystals for X-ray diffraction studies were grown from a diethyl ether solution at ambient temperature: yield 150.0 mg, 93%; mp 99−103 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 12.0 Hz, 2H), 7.71 (d, J = 12.0 Hz, 1H), 7.63 (t, J = 12.0 Hz, 1H), 7.59 (t, J = 6.0 Hz, 1H), 7.47 (t, J = 6.0 Hz, 1H), 7.41 (d, J = 6.0 Hz, 1H), 7.34 (t, J = 6.0 Hz, 1H), 7.22 (t, J = 12.0 Hz, 1H), 7.12 (t, J = 6.0 Hz, 2H), 7.06 (d, J = 6.0 Hz, 2H), 7.01 (d, J = 6.0 Hz, 2H,), 6.85 (d, J = 6.0 Hz, 2H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 177.69, 158.66, 143.61, 138.52, 138.01, 137.72, 136.28, 135.10, 134.13, 131.18, 130.70, 130.19, 129.35, 128.84, 127.86, 127.17, 127.01, 114.13, 55.56, 34.82, 31.74, 25.44, 22.81, 14.28; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 47.4 (br); FT-IR (cm^{-1} (ranked intensity)): 1606 (15), 1505 (2), 1431 (10), 1388 (4), 1294 (13), 1243 (3), 1145 (9), 1032 (6), 908 (12), 842 (5), 766 (14), 730 (11), 698 (1), 621 (8), 536 (7); high-resolution mass spectrometry (HRMS) electrospray ionization (ESI) calcd for $C_{26}H_{21}BNO_2$ $[M + H]^+$ 390.1664, found 390.1660; UV−vis (CH_2Cl_2) λ_{max} (237 nm) ε = 4000 L mol^{-1} cm^{-1}.

Synthesis of 8. At room temperature, a solution of diphenylketene (22.0 mg, 0.113 mmol; 1 mL) in CH_2Cl_2 was added to a solution of 7 (50.0 mg, 0.113 mmol; 2 mL) in CH_2Cl_2. The solution was stirred for 5 d until the solution became light yellow. The solvent was removed in vacuo to obtain a light yellow solid. The residue was washed with hexanes (2 × 1 mL) and dried in vacuo to give **8** as a white powder. Single crystals for X-ray diffraction studies were grown from a CH_2Cl_2 solution of **8** by vapor diffusion into hexanes: yield 54.0 mg, 75%; mp 187−189 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82−7.79 (m, 2H), 7.73−7.69 (m, 2H), 7.47−7.39 (m, 3H), 7.37−7.30 (m, 5H), 7.25−7.21 (m, 3H), 7.15−7.03 (m, 6H), 6.97−6.91 (m, 4H), 6.90−6.86 (m, 4H), 6.84−6.82 (m, 2H), 6.77−6.73 (m, 4H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 153.52, 148.32, 145.62, 144.00, 141.70, 140.52, 139.67, 139.53, 139.22, 138.94, 138.32, 135.97, 131.36, 130.84, 130.69, 130.59, 130.38, 129.87, 129.59, 128.01, 127.90, 127.71, 127.28, 127.14, 127.06, 127.02, 126.81, 126.58, 126.31, 126.06, 125.73; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 45.1 (br); FT-IR (cm^{-1} (ranked intensity)) 1597 (9), 1487 (8), 1437 (6), 1275 (1), 1223 (13), 1177 (11), 1065 (15), 1016 (5), 760 (10), 747 (4), 661 (2), 640 (14), 604 (12), 570 (7), 541 (3); high-resolution mass spectrometry (HRMS) electrospray ionization (ESI) calcd for $C_{48}H_{36}BO$ $[M + H]^+$ 639.2859, found 639.2857.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00497.

X-ray data, NMR, UV/vis, fluorescence, and FT-IR spectra (PDF)

Accession Codes

CCDC 1849479−1849487 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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