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The synthesis and characterization of phenylacetylene tripodal compounds containing boroxine cores

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Abstract—A convergent synthesis of phenylacetylene tripodal compounds containing boroxine cores has been accomplished. The boroxine cores are assembled in high yield either by chemical dehydration or ligand-facilitated trimerization of the corresponding monomeric boronic acids.

The tripodal molecular architecture is a common structural motif found in such diverse areas as dendrimers,[1] hyperbranched polymers,[2] receptors for small molecule recognition,[3] and catalysts.[4] Boroxines, the dehydration product of boronic acids, have found commercial use in such diverse areas as flame retardant materials,[5] dopants that enhance lithium ion transference in polymer electrolytes,[6] and recently as boronic acid alternatives in Suzuki–Miyaura coupling reactions.[7] Our group is interested in utilizing boroxine rings to construct conjugated C_3-symmetric materials. From a molecular design perspective, boroxine-based organic materials[8] are of interest because they provide rapid synthetic entry into tripodal architectures. Furthermore, the boroxine's Lewis acidity[9] and rich ligand chemistry provides additional opportunities to functionalize boroxine based-materials through noncovalent interactions. In this work, we have synthesized conjugated boronic acid monomers that are efficiently converted to boroxine containing materials (Fig. 1). In addition, we investigate ligand-facilitated boroxine formation as an alternative to dehydration in the construction of the central boroxine ring.

The conjugated synthetic precursors are synthesized convergently with the boron functionality being introduced late in the synthesis. The boronate ester is converted to a boronic acid, and upon workup, the boronic acid is dehydrated to the boroxine. As an alternative to dehydration, arylboronic acids can rapidly be converted to boroxine·ligand adducts by stirring at room temperature with a suitable ligand.[10,11] Although binding of Lewis bases with preformed boroxines is well established, utilizing the low temperature conversion of monomeric boronic acids to boroxine·ligand adducts as a means of assembling tripodal architectures has not been demonstrated. Ligand-facilitated formation of boroxine takes advantage of the high thermodynamic stability of the boroxine·ligand complex relative to the monomeric boronic acid.[12]

The synthesis of boroxine **1** and **1**·pyridine is shown in Scheme 1. Using standard Sonogashira–Hagihara coupling methodology,[13] commercially available 4-*tert*-butylphenyl acetylene was coupled to pinacol protected 4-iodophenyboronic acid. Exchange of the pinacol group for diethanolamine followed by acidic hydrolysis afforded the boronic acid.[14] The addition of a drying agent, calcium chloride, to a toluene solution of the boronic acid promotes dehydration to boroxine.

The syntheses of branched boroxines **2** and **3** are outlined in Schemes 2 and 3. 1,3,5-Tribromobenzene is converted to disubstituted derivative **7**. Compound **7** is borylated with bis(pinacolato)diboron to yield compound **8** in 46% isolated yield. Conversion of **8** to boroxine **2** was inefficient. After drying a toluene solution of boronic acid **9** over calcium chloride, NMR analysis shows a mixture of **2** and **9**. Boroxine formation is facilitated by the addition of pyridine (1.5 equiv relative to the theoretical yield of boroxine). After stirring, excess

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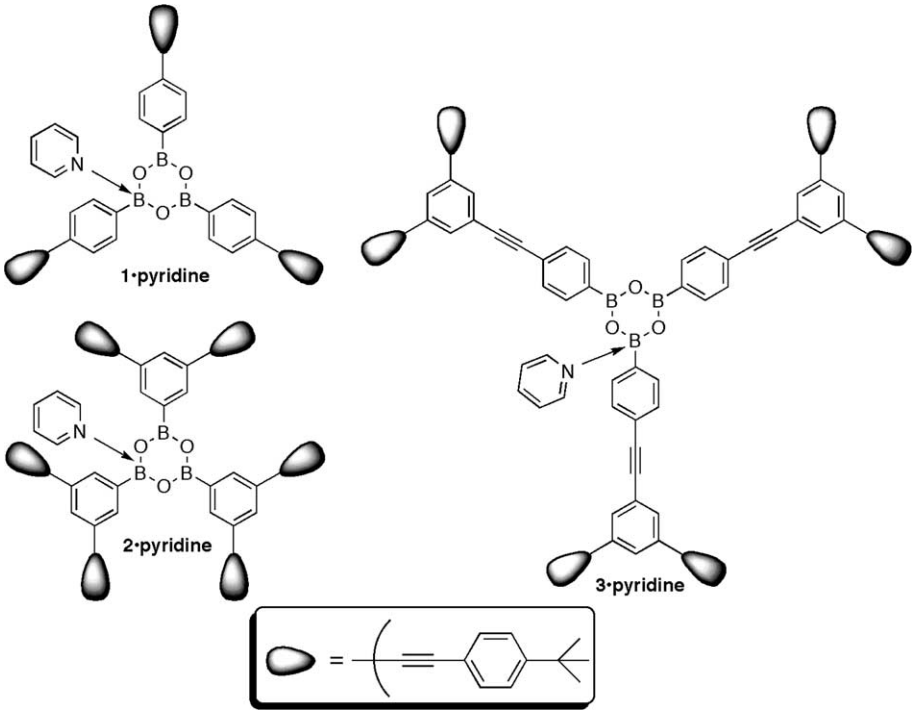
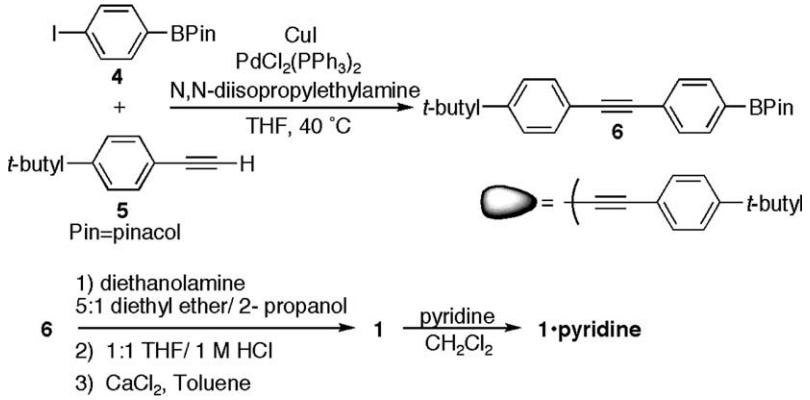


Figure 1. Conjugated boroxine core compounds **1**·pyridine, **2**·pyridine, and **3**·pyridine.



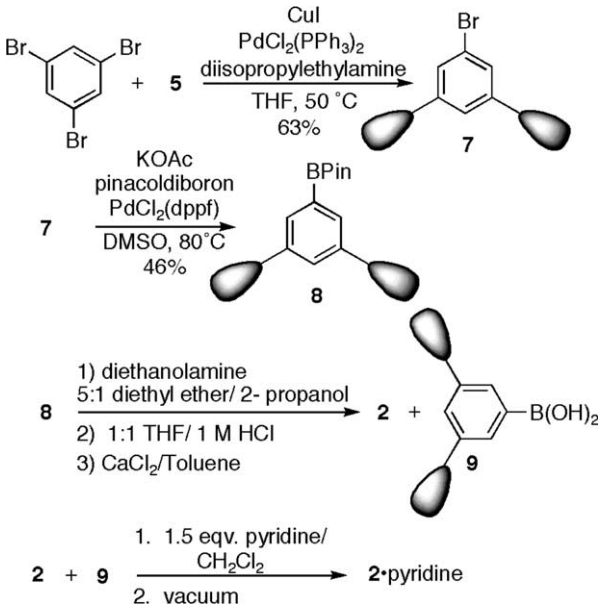
Scheme 1. Synthesis of compound **1**·pyridine.

pyridine is removed under vacuum leaving the 1:1 boroxine **2**·pyridine adduct.

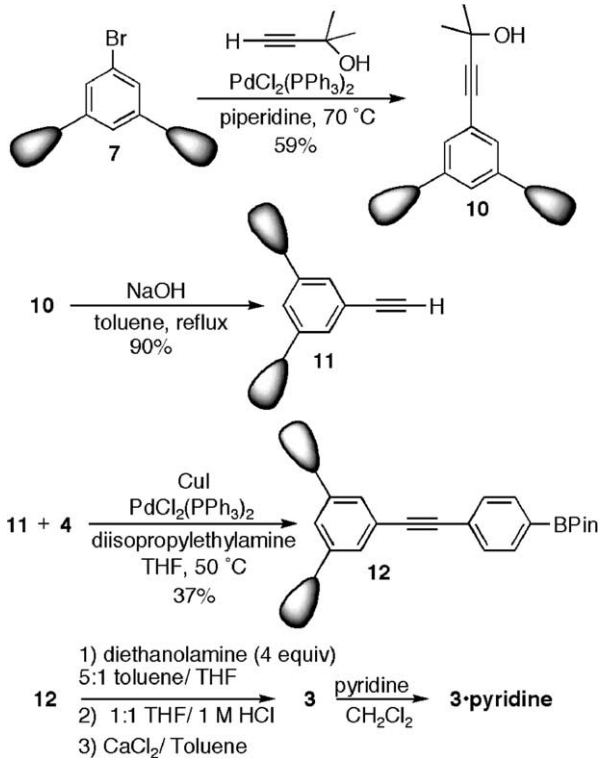
Compound **7** can be further elaborated using 2-methyl-3-butyn-2-ol. After deprotection under basic conditions,[15] acetylene **11** is coupled to 4-iodophenylboronic acid pinacol ester **4** giving compound **12** in 37% isolated yield (Scheme 3). After deprotection of **12**, the boronic acids are taken up in toluene and smoothly converted to the boroxine **3** by drying over calcium chloride.

The solubility of these compounds is noteworthy. Boroxines **1** and **3** are initially soluble in chloroform but precipitate on standing. This is likely due to the formation of π-stacked aggregates.[16] In contrast, the boroxine·pyridine adducts are highly soluble in chloroform. Addition of a stoichiometric volume of pyridine to a heterogeneous mixture of either monomeric boronic acid or boroxine that has precipitated from a chloroform solution, results in a homogeneous solution consisting of boroxine·pyridine adduct. The introduction of the pyridine ligand drives the formation of the boroxine adduct and this adduct shows a concomitant increase in solubility. As in other boroxine·pyridine adducts,[8b,10a,d,11] the pyridine ligand is in fast exchange on the NMR timescale and the observed chemical shift of the *ortho* protons are a weighted average of the ligated and unligated forms.

The UV–vis absorption spectra of boronate ester **8**, in the presence of pyridine, and **2**·pyridine are shown in Figure 2. As can be seen from the data, there is no broadening or red shifting of the absorption maxima (291 nm, 308 nm) going from a boronate ester to the tripodal boroxine. This suggests that there are no significant electronic perturbations caused by boroxine ring



Scheme 2. Synthesis of compound **2**·pyridine.



Scheme 3. Synthesis of compound **3**·pyridine.

incorporation as compared to the corresponding boronate ester. As expected, the molar extinction coefficient of **2**·pyridine tripodal assembly increases relative to the monomeric boronate ester.

In conclusion, a series of phenylacetylene boroxine core compounds have been convergently synthesized. The boroxine core is easily formed by one of two synthetic methods, dehydration or ligand-facilitated trimerization, and functions as a tripodal scaffold.

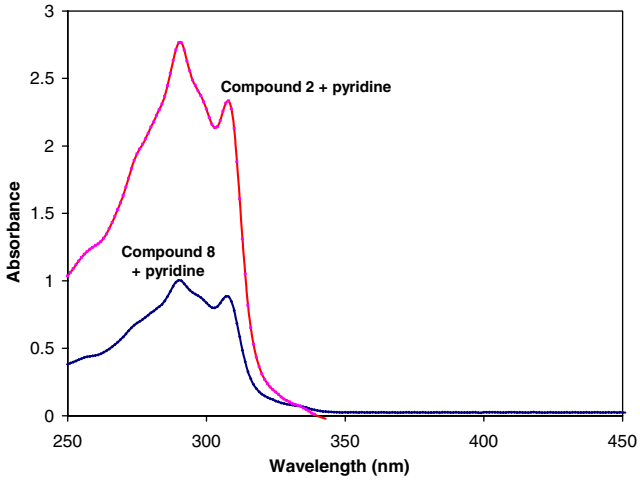


Figure 2. UV–vis absorption spectra of boronate ester **8** (in the presence of pyridine) and boroxine·pyridine adduct **2**·pyridine in dichloromethane. The spectra are normalized to 15 μM.

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Supplementary data

Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.10.033.

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