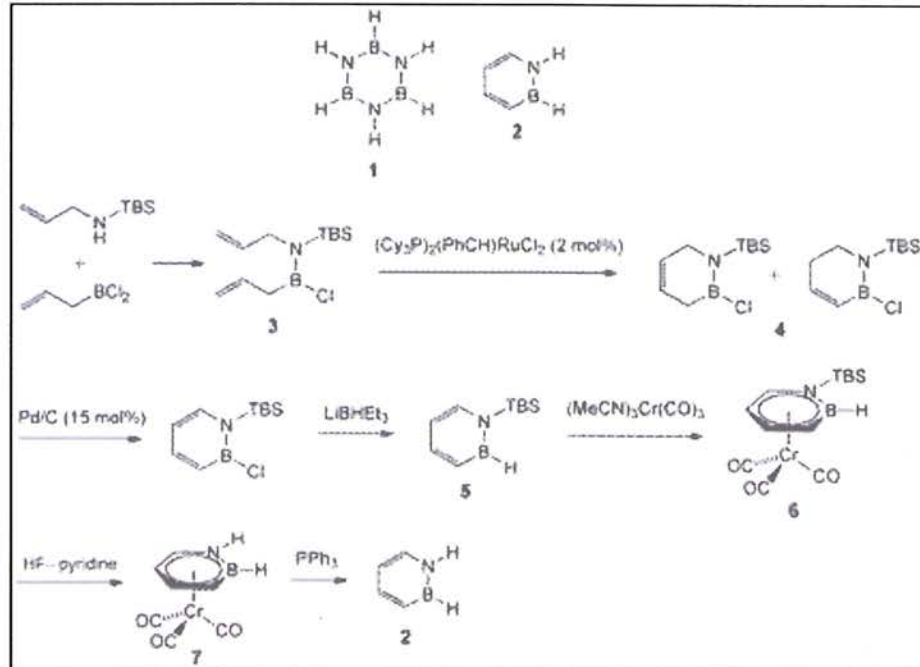


# Noteworthy Chemistry

February 23, 2009

- An elusive aromatic hybrid organic–inorganic benzene has been isolated
- Ion association generates highly fluorescent organic nanoparticles
- Expediently extract biodiesel from sunflower seeds
- Silver–gold core–shell nanoparticles supported on porous solids
- Clay fractionation leads to optical clarity in polymer nanocomposites
- A palladium–curcumin complex may help fight prostate cancer
- Asymmetric synthesis of substituted oxetanes with sulfur ylides

**An elusive aromatic hybrid organic–inorganic benzene has been isolated.** Borazine (1), benzene's isoelectronic inorganic counterpart, exhibits the remarkable feature of aromaticity. Although borazine was reported in 1926, the corresponding hybrid structure 1,2-dihydro-1,2-azaborine (2) has eluded synthesis and characterization. D. A. Dixon, S.-Y. Liu, and coauthors at the University of Alabama (Tuscaloosa) and the University of Oregon (Eugene) report an innovative synthesis of 2. Their accomplishment demonstrates that 2 is not only isolable but has remarkable stability that is consistent with substantial aromatic character.



In the figure, TBS is *tert*-butyldimethylsilyl and Cy is cyclohexyl. In the first step of the synthesis, allylboron dichloride is coupled with a protected allylamine to yield a diene (3) that contains the critical B–N bond. The conformation of 3 provides the appropriate structure for ring-closing metathesis to give two isomers of heterocycle 4. Dehydrogenation of 4 followed by treatment with  $\text{LiBHET}_3$  incorporates the desired B–H functionality (5).

Ordinarily, removing the N-protecting group would lead directly to **2**. However, attempts to isolate **2** in this way were unsuccessful, and the authors were forced to treat **5** with  $[\text{Cr}(\text{CO})_3]$  as a temporary “protecting group” to yield complex **6**. The N-protecting group could then be removed to install the necessary N–H bond in **7** as the precursor to **1**. Decomplexation of **7** gives the target organic–inorganic hybrid **2**.

A solution of **2** shows no appreciable degradation when heated at 60 °C for 5 days. The authors characterized **2** by using standard spectral techniques and found the data to be consistent with their proposed structure for 1,2-dihydro-1,2-azaborine.

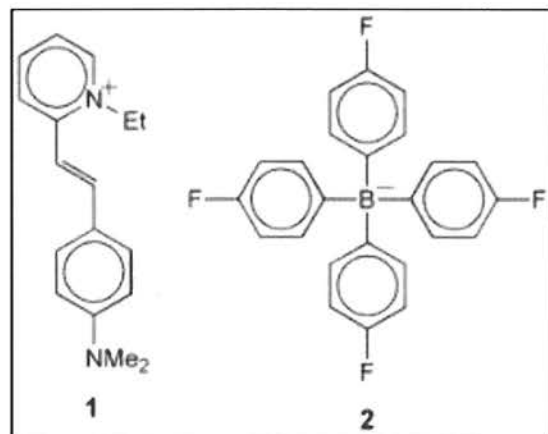
An important part of this study was to determine the aromatic character of **2** because the all-inorganic heterocycle borazine **1** is considered to be less aromatic than benzene. Several facts and measurements support a considerable aromatic character for **2**. Previously synthesized 1,2-azaborines underwent electrophilic aromatic substitution reactions readily. The authors recently provided structural data showing that 1,2-azaborines have delocalized structures consistent with aromaticity (Abbey, E. R.; Zakharov, L. N.; Liu, S.-Y. *J. Am. Chem. Soc.* **2008**, *130*, 7250–7252).

Although the authors could not determine the crystal structure of **2**, they obtained the structure of its  $[\text{Cr}(\text{CO})_3]$  complex **7**, which showed similar bond lengths when compared with the corresponding benzene  $[\text{Cr}(\text{CO})_3]$  complex. They also determined the binding energy of the 1,2-azaborine ring to  $[\text{Cr}(\text{CO})_3]$  to be  $-54.4$  kcal/mol—essentially the same as the value for the benzene complex.

As part of this study, the authors computed the resonance stabilization energy of **2** to be 21 kcal/mol,  $\sim 13$  kcal/mol less than that of benzene. Based on the accumulated data, they consider **2** to be significantly aromatic. (*Angew. Chem., Int. Ed.* **2009**, *48*, 973–977; **W. Jerry Patterson**)

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**Ion association generates highly fluorescent organic nanoparticles.** Luminescent nanoparticles are potentially useful for making light-emitting diodes, organic lasers, sensors, and the like. To realize this potential, versatile processes for producing such nanoparticles must be developed. H. Yao\*, M. Yamashita, and K. Kimura at the University of Hyogo (Japan) developed an ion-association technique for preparing organic nanoparticles that fluoresce efficiently in the solid state.



When 2-[4-(dimethylamino)styryl]-1-ethylpyridinium (**1**), a cationic luminogen, is mixed with an anionic borate such as tetrakis(4-fluorophenyl)borate (**2**) in the presence of aqueous poly(vinylpyrrolidone), nanoparticles with  $\sim 30$ – $100$ -nm diam are formed as a result of the electrostatic interaction between ion pairs. Whereas the iodide salt of **1** in water is virtually nonluminescent, the nanoparticles of the **1–2** pair are highly emissive; their fluorescence quantum yield is  $>20$ -fold higher than that of the iodide.

The researchers believe that the fluorescence comes from an intramolecular charge-transfer excited state stabilized by the matrix of **2**. They also conjecture that the emission enhancement is caused by the high rotational resistance around the single bond in **1** and the effect of matrix polarity that suppresses nonradiative processes. (*Langmuir* **2009**, *25*, 1131–2237;