DOI: 10.1002/ange.200805554

Boron Heterocycles

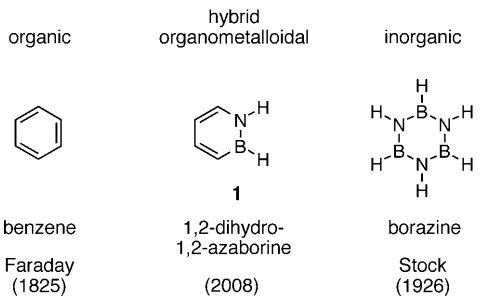
# A Hybrid Organic/Inorganic Benzene**

*Adam J. V. Marwitz, Myrna H. Matus, Lev N. Zakharov, David A. Dixon,* and Shih-Yuan Liu**

*Dedicated to Professor Gregory C. Fu on the occasion of his 45th birthday*

Benzene ($c$-$C_6H_6$) is arguably one of the most fundamentally significant small molecules in chemistry. First discovered by Faraday in 1825,[1] the study of benzene introduced the basic concept of aromaticity and delocalization.[2] In addition to its fundamental importance, benzene and its derivatives (arenes) are ubiquitous in chemical research with numerous applications ranging from biomedical research to materials science.[3] The inorganic isoelectronic relative of benzene, borazine ($c$-$B_3N_3H_6$),[4] has also played a pivotal role in fundamental as well as applied chemistry. The isoelectronic and isostructural relationship between the B–N and C=C bond and its consequence on the aromaticity of borazine has been a topic of discussion.[5] From a more applied perspective, borazine serves as a precursor to BN-based ceramic materials.[6] More recently, borazine has been implicated in chemical hydrogen storage applications because it is formed as an intermediate in the hydrogen release from ammonia–borane.[7] Both benzene and borazine have been known for more than 80 years, and consequently, their chemical and physical properties have been thoroughly investigated. The corresponding organic/inorganic (or organometalloidal) hybrid structure containing carbon, boron, and nitrogen, that is, 1,2-dihydro-1,2-azaborine **1**, has thus far eluded characterization.

The development of boron–nitrogen heterocycles such as 1,2-dihydro-1,2-azaborines (from hereon in, abbreviated as 1,2-azaborines) has been a relatively unexplored area of research.[8] Dewar and White pioneered the chemistry of monocyclic and ring-fused polycyclic 1,2-azaborine derivatives in the 1960s.[9] Recently, contributions by the groups of Ashe,[10] Piers,[11] and Paetzold,[12] as well as our group[13] have further advanced the preparation of novel BN heterocycles and sparked a renewed interest in the chemistry and properties of these compounds.[14] Despite the advances achieved to date, and given the powerful tools made available by modern chemical synthesis, it is surprising that a simple heterocycle such as the parent 1,2-dihydro-1,2-azaborine **1** has remained elusive. Dewar attempted its synthesis and isolation in 1967 but ultimately concluded that it "seems to be a very reactive and chemically unstable system, prone to polymerization and other reactions."[15]




Herein, we describe the first isolation and characterization of 1,2-dihydro-1,2-azaborine. Its successful preparation allows a direct comparison of the physical and spectroscopic properties of the series of an organic, inorganic, and now, an organometalloidal benzene. The present study demonstrates that 1,2-dihydro-1,2-azaborine **1** is not only isolable but it actually exhibits remarkable stability, consistent with substantial aromatic character. Our experimentally determined structural and spectroscopic properties are consistent with values derived from high-level computations.

Scheme 1 illustrates our synthetic route to compound **1**. Coupling of the in situ-generated allylboron dichloride with *tert*-butyldimethylsilyl allyl amine (TBS allyl amine) furnished diene **2**. Ring-closing metathesis of this intermediate with the first-generation Grubbs catalyst produced an isomeric mixture of **3** and **3′** (60:40 ratio) in 82% yield. Dehydrogenation of this mixture was carried out in the presence of catalytic amounts of Pd/C to generate **4**. Treatment of heterocycle **4** with $LiBHEt_3$ installed the B–H functionality to give **5** in quantitative yield. Complexation of 1,2-azaborine **5** to $\{Cr(CO)_3\}$ produced the piano-stool adduct **6**.[16] Subsequent removal of the *N*-protecting group gave **7** in 76% yield. Finally, decomplexation of **1** from $\{Cr(CO)_3\}$ was accomplished using triphenylphosphine.

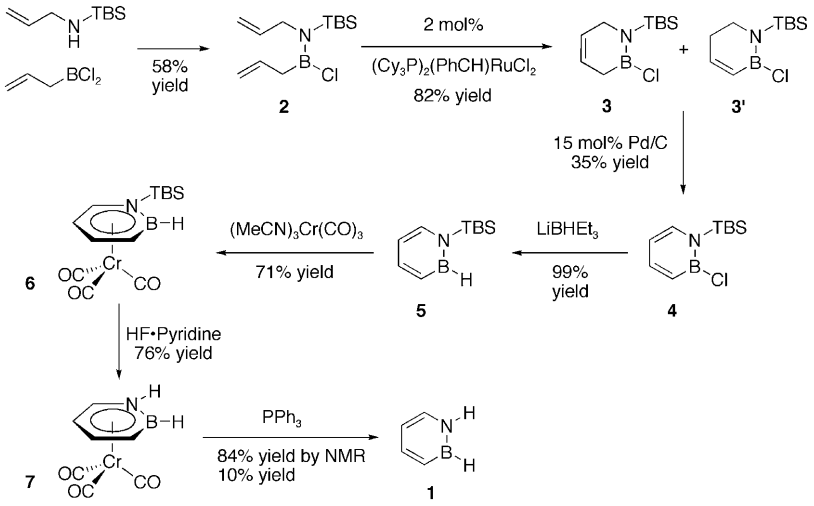
The use of $\{Cr(CO)_3\}$ as a temporary "protecting group" was necessary because efforts toward cleaving the N–TBS bond directly from **5** were unsuccessful. Compound **1** proved to be difficult to isolate, owing to its high volatility. However, we ultimately accomplished its isolation (10% yield) by fractional vacuum transfer in the presence of a low-boiling

[*] M. H. Matus, Prof. Dr. D. A. Dixon
Department of Chemistry, University of Alabama
Tuscaloosa, AL 35487 (USA)
E-mail: dadixon@as.ua.edu
A. J. V. Marwitz, Dr. L. N. Zakharov, Prof. Dr. S.-Y. Liu
Department of Chemistry, University of Oregon
Eugene, OR 97403-1253 (USA)
E-mail: lsy@uoregon.edu

[**] Correspondence concerning X-ray crystallography should be directed to Lev Zakharov (lev@uoregon.edu). Correspondence concerning computational calculations should be directed to David Dixon. Funding was provided by the U.S. Department of Energy (S.Y.L., DE-FG36-08GO18143; D.A.D., DE-FC36-05GO15059), and the National Science Foundation (A.J.V.M., DGE-0549503). We thank Ms. Raluca Craciun for preparing the ESP maps.

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200805554.




***Scheme 1.*** Synthesis of 1,2-dihydro-1,2-azaborine **1**.

reaction solvent, isopentane. The inherent efficiency of the decomplexation reaction (84% yield) was measured by $^1$H NMR spectroscopy against an internal standard. The melting point of **1** is −45 °C, which is slightly higher than that of borazine (−58 °C) but considerably lower than that of benzene (5 °C). We found 1,2-dihydro-1,2-azaborine **1** to be a relatively stable heterocycle. $^1$H NMR spectroscopy of a 0.7 M solution of **1** in $CD_2Cl_2$ showed no appreciable degradation when the solution was heated to 60 °C for five days. Furthermore, **1** is stable to chromatography on silica gel and is relatively nonpolar ($R_f = 0.4$ with pentane as eluent).

We characterized compound **1** by using NMR, UV/Vis, and IR spectroscopy, and high-resolution mass spectrometry. The data are consistent with the proposed structure of **1**. Figure 1 depicts the $^1$H NMR spectrum of heterocycle **1**. The

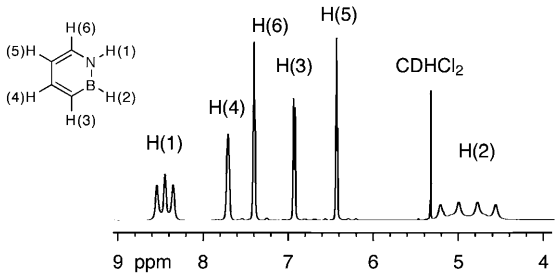



***Figure 1.*** $^1$H NMR spectrum of **1** in $CD_2Cl_2$.

proton signals were unambiguously assigned through 2D NMR spectroscopy experiments.[17] The C–H resonances all lie in the aromatic region and display the characteristic pattern of a 1,2-azaborine. The B–H resonance appears upfield of the other resonances and is split into a broad quartet ($^1J_{BH} = 130$ Hz) by the $^{11}$B atom ($S = 3/2$). The coupling of the N–H proton with the $^{14}$N nucleus ($S = 1$) results in a triplet ($^1J_{NH} = 57$ Hz) that is observed for solutions of **1** in $CD_3CN$, $C_6D_6$, $CD_3OD$, and $CD_2Cl_2$.

Figure 2 shows a direct comparison of the UV/Vis absorption spectra of benzene, borazine, and **1**.[18] The spectrum for compound **1** displays $\lambda_{max}$ at 269 nm ($\varepsilon = 15632\ M^{-1}cm^{-1}$), with two smaller transitions at 219 nm ($\varepsilon = 8495\ M^{-1}cm^{-1}$) and at 205 nm ($\varepsilon = 7459\ M^{-1}cm^{-1}$). The absorbance at 269 nm is only slightly red-shifted relative to the α band of benzene (255 nm, $\varepsilon = 977\ M^{-1}cm^{-1}$), but absorbs much more strongly than benzene. Benzene's strongest absorption band is located at 208 nm ($\varepsilon = 12380\ M^{-1}cm^{-1}$). In contrast to benzene and 1,2-azaborine **1**, the absorption spectrum of borazine shows only a very weak band at 203 nm ($\varepsilon = 1299\ M^{-1}cm^{-1}$) and negligible absorbance at higher wavelengths. The electronic spectrum of **1** is consistent with a delocalized aromatic

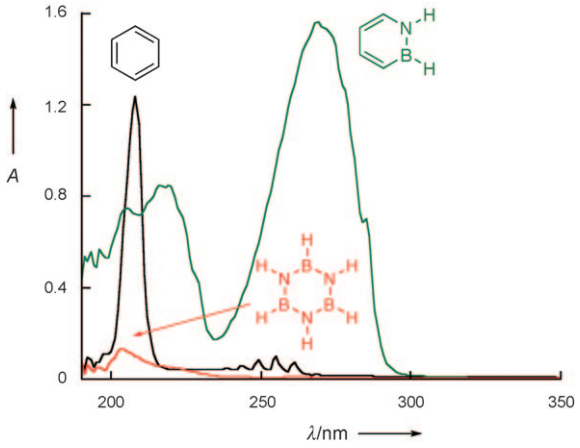


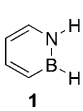
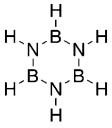

***Figure 2.*** Absorption spectra of **1**, benzene, and borazine. All substrates are $10^{-4}$ M in pentane.

system and differs substantially from the behavior exhibited by borazine.

Our experimentally determined spectroscopic data are supported by electronic structure calculations.[19] The chemical shifts in $^1$H, $^{13}$C, $^{11}$B, and $^{14}$N NMR spectroscopy of benzene, compound **1**, and borazine were calculated at the density functional theory (DFT) B3LYP/Alhrichs-vtzp level (see Table S1 in the Supporting Information). The excitation energies and oscillator strengths for the prediction of the UV/Vis spectra of benzene, 1,2-azaborine **1**, and borazine were calculated with time dependent DFT (TD-DFT) at the B3LYP/aug-cc-pVDZ//MP2/cc-pVTZ and B3LYP/aug-cc-pVTZ//MP2/cc-pVTZ levels, and with equations of motion CCSD (EOM-CCSD/aug-cc-pVDZ//MP2/cc-pVTZ) level (See Table S2 in the Supporting Information). The IR stretching frequencies of the benzene triad were calculated at the MP2/cc-pVTZ level (see Table S3 in the Supporting Information). The calculated spectroscopic signatures agree well with our experimental results, thus further supporting our structural assignment of compound **1**.

The aromaticity of benzene and borazine has been a topic of intense discussion, and borazine is generally considered substantially less aromatic than benzene.[5] What is the aromatic character of the organic/inorganic hybrid **1**? Ashe and co-workers showed that 1,2-azaborines readily undergo electrophilic aromatic substitution reactions.[20] We recently provided structural data highlighting that 1,2-azaborines have delocalized structures consistent with aromaticity.[13b] To complete the analysis, Table 1 contains the magnetic and

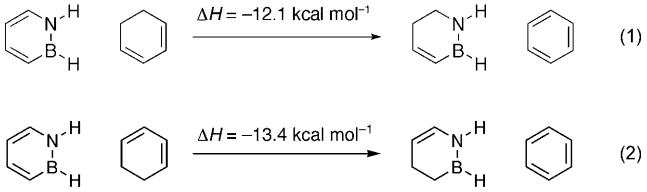
***Table 1:*** Chemical shift and stabilization energy data for benzene, 1,2-azaborine **1**, and borazine.[a]

| Entry | | |  **1** |  |
|---|---|---|---|---|
| 1 | δ(N–H, $^1$H NMR) | | 8.44,[b] [7.8] | 5.63,[b] [5.3] |
| 2 | δ(B–H, $^1$H NMR) | | 4.9,[b] [5.4] | 4.4,[b] [5.0] |
| 3 | NICS (0) | [−8.76] | [−5.62] | [−2.02] |
| 4 | NICS (1) | [−10.39] | [−7.27] | [−3.01] |
| 5 | RSE [kcal mol$^{-1}$] | [34.1] | [21 (±2)] | [c] |
| 6 | $\Delta H_{f(298)}$ [kcal mol$^{-1}$] | [20.5] | [3.0] | [−119.0] |

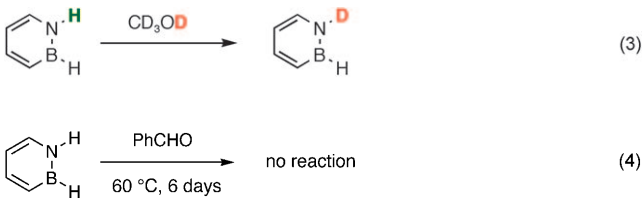
[a] Numbers in brackets are calculated values. [b] Experimental chemical shift [ppm] in $CD_2Cl_2$. [c] Value of 10.0 kcal mol$^{-1}$ taken from reference [5a] on the basis of a different reaction scheme.

energetic data of 1,2-azaborine **1** together with those data for benzene and borazine for direct comparison. The N–H and B–H chemical shifts of 1,2-azaborine **1** are significantly downfield shifted compared to the corresponding signals for borazine (Table 1, entries 1,2). The nucleus-independent chemical shift (NICS)[21] values of benzene, 1,2-azaborine **1**, and borazine indicate a trend of decreasing aromaticity going from benzene to borazine. These chemical shift patterns are consistent with 1,2-azaborine possessing substantial aromatic character. Finally, we have predicted the resonance stabilization energy (RSE)[22] of 1,2-azaborine **1** to be 21 kcal mol$^{-1}$ (Table 1, entry 5). This value was derived computationally (see the Supporting Information for details) through Equations (1) and (2), which reveal that the RSE of 1,2-azaborine **1** is approximately 13 kcal mol$^{-1}$ less than that of benzene (RSE = 34.1 kcal mol$^{-1}$). The heat of formation of **1** (Table 1, entry 6) was calculated using the same accurate approach used for predicting the heats of formation of benzene and borazine.[23] Thus, by all accounts (reactivity, structure, chemical shift, and stabilization energy), 1,2-azaborines can be considered significantly aromatic.

We carried out preliminary reactivity studies of heterocycle **1**. In particular, we were interested in determining




whether the N–H proton is protic and the B–H group is hydridic. The N–H functionality in **1** undergoes a deuterium exchange in $CD_3OD$ [Eq. (3)]. The disappearance of the N–H resonance in the $^1$H NMR spectrum of **1** was monitored over the course of approximately 24 h. The rate constant for exchange in $CD_3OD$ was determined to be $k_{HD} = 7(\pm 2) \times 10^{-7}\,M^{-1}s^{-1}$. The B–H group is typically hydridic in character. For instance, Fu and co-workers demonstrated that the negatively charged 1*H*-boratabenzene reduces *n*-dodecanal to dodecanol.[24] However, no reaction between **1** and benzaldehyde occurred over the course of several days at 60 °C [Eq. (4)]. In contrast, complete consumption of benzaldehyde with borazine was observed within 24 h, furnishing reduced benzaldehyde derivatives. The unreactive nature of **1** relative to borazine indicates that the chemical reactivity of **1** more closely resembles that of benzene than borazine.




Although we were unable to determine the crystal structure of **1**, we were able to obtain the structure of its chromium(0) tricarbonyl adduct **7**, and thus assess the coordinating ability of **1**. Single crystals of **7** suitable for X-ray diffraction were grown from an ether solution of **7** by slow evaporation.[25] Figure 3 lists selected structural parameters of

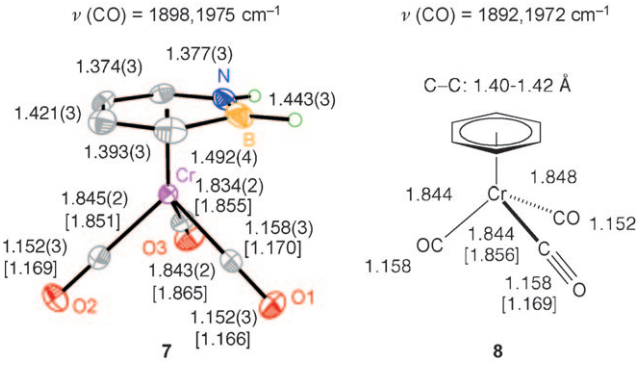



***Figure 3.*** Molecular structure of **7**, in direct comparison with the known benzene chromium(0) tricarbonyl complex **8**. Numbers in brackets are computed values optimized at the B3LYP/DGDZVP2 level.

complex **7** together with the known bond lengths for the benzene chromium(0) tricarbonyl complex **8**[26] for direct comparison. The geometries in **7**, including the Cr–CO and C–O distances, are strikingly similar to that for the benzene analogue **8**, indicating that the coordination behavior of 1,2-azaborine **1** is similar to that of benzene. This is further supported by the nearly identical carbonyl stretching frequencies between the two complexes measured by FT-IR

spectroscopy. The binding energy of the 1,2-azaborine ring to $\{Cr(CO)_3\}$ in **7** is calculated at the DFT B3LYP/DZVPZ level to be $-54.4$ kcal mol$^{-1}$, which is essentially the same as the value for the benzene derivative ($-54.9$ kcal mol$^{-1}$). On the other hand, the binding energy of the corresponding borazine complex is only $-42.7$ kcal mol$^{-1}$.

Electronic structure calculations of compound **1** at the B3LYP/DZVP2 level show that, in contrast to benzene and borazine, the HOMO of 1,2-azaborine is not degenerate. The HOMO–LUMO gap in **1** (5.32 eV) is smaller than those for benzene (6.55 eV) and borazine (7.91 eV). This trend is consistent with the electronic spectra (Figure 2). The orbital diagram of the HOMO of **1** is shown in Figure 4 A. We also

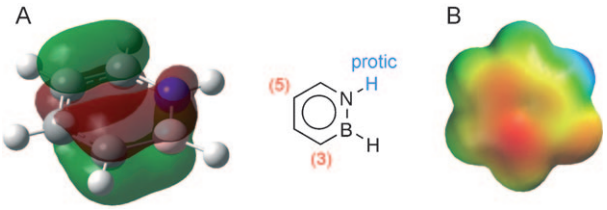



***Figure 4.*** A) HOMO of 1,2-azaborine **1**. B) Electrostatic potential surface of **1** at the 0.002 electron a.u.$^{-3}$ density iso-contour level ($-13.6$ to 39.9 kcal mol$^{-1}$).

determined the charge distribution of **1** in the form of an electrostatic potential (ESP) surface (Figure 4 B). The calculated electronic structure reveals substantial electron density at the 3 and 5 positions of the 1,2-azaborine ring, which is consistent with the experimental results, in which electrophilic aromatic substitutions occur exclusively at these positions of the heterocycle. The ESP diagram shows a positive electrostatic potential (blue color) at the N–H group, which is consistent with the observed protic nature of the N–H proton.

In summary, we prepared 1,2-dihydro-1,2-azaborine **1**, a hybrid organic/inorganic benzene that had thus far eluded characterization. The structural, spectroscopic, and chemical data presented in this work were fully supported by high-level calculations, and indicated that 1,2-dihydro-1,2-azaborine is a stable aromatic molecule with features that are distinct from its "organic" and "inorganic" counterparts. Given the importance and ubiquity of benzene derivatives in scientific research, the development of benzene mimics such as 1,2-azaborines will undoubtedly lead to new discoveries. The synthesis and characterization of the parent compound of this family of heterocycles marks an important milestone and will enhance our fundamental understanding of BN heterocycles in areas such as biomedical research and materials science.

## Experimental Section

**1**: In a glove box (under a nitrogen atmosphere), complex **7** (0.150 g, 0.698 mmol), triphenylphosphine (0.915 g, 3.49 mmol), and isopentane (3.0 mL) were combined in a Schlenk tube and sonicated at room temperature for 3 h. Isopentane and **1** were transferred under vacuum to a cold trap at $-78$ °C. Residual isopentane was removed under vacuum to provide **1** as a clear and colorless liquid (0.006 g, 10 %, yield determined by $^1$H NMR spectroscopy in $CD_3OD$ with hexamethylbenzene as an internal standard). m.p. $-46$–$-45$ °C; $^1$H NMR (600 MHz, $CD_2Cl_2$): $\delta = 8.44$ (t, $^1J_{NH} = 57$ Hz, 1H), 7.70 (br app. t, 1H), 7.40 (app. t, $^3J_{HH} = 6.5$ Hz, 1H), 6.92 (d, $^3J_{HH} = 10.7$ Hz, 1H), 6.43 (t, $^3J_{HH} = 6.3$ Hz, 1H), 4.9 ppm (br q, $^1J_{BH} = 128$ Hz, 1H); $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta = 144.5$, 134.7, 131.6, 112.1 ppm; $^{11}$B NMR (192.5 MHz, $CD_2Cl_2$): $\delta = 31.0$ ppm (d, $^1J_{BH} = 131$ Hz); FT-IR (thin film): $\tilde{\nu} = 3398$, 3027, 3008, 2525, 1613, 1533, 1453, 1427, 1350, 1216, 1162, 1109, 894, 820, 715, 579 cm$^{-1}$; UV/Vis (pentane): $\lambda_{max} = 269$ nm. HRMS (EI) calcd for $C_4H_6BN$ ($M^+$): 79.059330; found: 79.059269.

Received: November 13, 2008
Published online: December 22, 2008

**Keywords:** aromaticity · benzene · boron · density functional calculations · heterocycles

[1] M. Faraday, *Philos. Trans. R. Soc. London* **1825**, *115*, 440–466.
[2] a) P. v. R. Schleyer, *Chem. Rev.* **2001**, *101*, 1115–1117; b) P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3433–3435.
[3] D. Astruc in *Modern Arene Chemistry* (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2002**, pp. 1–19.
[4] a) A. Stock, E. Pohland, *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 2210–2215; b) D. F. Gaines, J. Borlin in *Boron Hydride Chemistry* (Ed. E. L. Muetterties), Academic Press, New York, **1975**, pp. 241–272.
[5] a) P. v. R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin, O. L. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669–12670; b) B. Chiavarino, M. E. Crestoni, A. Di Marzio, S. Fornarini, M. Rosi, *J. Am. Chem. Soc.* **1999**, *121*, 11204–11210; c) R. Islas, E. Chamorro, J. Robles, T. Heine, J. C. Santos, *Struct. Chem.* **2007**, *18*, 833–839.
[6] a) M. Mokhtari, H. S. Park, H. W. Roesky, S. E. Johnson, W. Bolse, J. Conrad, W. Plass, *Chem. Eur. J.* **1996**, *2*, 1269–1274; b) P. J. Fazen, E. E. Remsen, J. S. Beck, P. J. Carroll, A. R. McGhie, L. G. Sneddon, *Chem. Mater.* **1995**, *7*, 1942–1956.
[7] a) T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262–8264; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116–8118; b) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626.
[8] a) A. J. Fritsch, *Chem. Heterocycl. Compd.* **1977**, *30*, 381–440; b) W. E. Piers, M. J. D. Bosdet, *Can. J. Chem.* **2009**, *87*, 8–29.
[9] a) G. C. Culling, M. J. S. Dewar, P. A. Marr, *J. Am. Chem. Soc.* **1964**, *86*, 1125–1127; b) D. G. White, *J. Am. Chem. Soc.* **1963**, *85*, 3634–3636.
[10] a) A. J. Ashe III, X. Fang, X. Fang, J. W. Kampf, *Organometallics* **2001**, *20*, 5413–5418; b) A. J. Ashe III, X. Fang, *Org. Lett.* **2000**, *2*, 2089–2091; c) J. Pan, J. W. Kampf, A. J. Ashe III, *Organometallics* **2008**, *27*, 1345–1347.
[11] a) C. A. Jaska, W. E. Piers, R. McDonald, M. Parvez, *J. Org. Chem.* **2007**, *72*, 5234–5243; b) C. A. Jaska, D. J. H. Emslie, M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *J. Am. Chem. Soc.* **2006**, *128*, 10885–10896; c) M. J. D. Bosdet, C. A. Jaska, W. E. Piers, T. S. Sorensen, M. Parvez, *Org. Lett.* **2007**, *9*, 1395–1398; d) M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *Angew. Chem.* **2007**, *119*, 5028–5031; *Angew. Chem. Int. Ed.* **2007**, *46*, 4940–4943.
[12] P. Paetzold, C. Stanescu, J. R. Stubenrauch, M. Bienmueller, U. Englert, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2632–2640.
[13] a) A. J. V. Marwitz, E. R. Abbey, J. T. Jenkins, L. N. Zakharov, S.-Y. Liu, *Org. Lett.* **2007**, *9*, 4905–4908; b) E. R. Abbey, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 7250–7252.
[14] Z. Liu, T. B. Marder, *Angew. Chem.* **2008**, *120*, 248–250; *Angew. Chem. Int. Ed.* **2008**, *47*, 242–244.

[15] K. M. Davies, M. J. S. Dewar, P. Rona, *J. Am. Chem. Soc.* **1967**, *89*, 6294 – 6297.
[16] J. Pan, J. W. Kampf, A. J. Ashe III, *Organometallics* **2006**, *25*, 197 – 202.
[17] See the Supporting Information for the COSY and HETCOR spectra of **1**.
[18] The electronic spectra of benzene, compound **1**, and borazine were measured under identical conditions ([substrate] = $10^{-4}$ M in pentane) to ensure a direct comparison.
[19] For computational details of this work, see the Supporting Information. For previously reported calculations on compound **1**, see: a) T. Kar, D. E. Elmore, S. Scheiner, *J. Mol. Struct. (Theochem)* **1997**, *392*, 65 – 74; b) M. Kranz, T. Clark, *J. Org. Chem.* **1992**, *57*, 5492 – 5500; c) S. T. Massey, R. W. Zoellner, *Int. J. Quantum Chem.* **1991**, *39*, 787 – 804.
[20] J. Pan, J. W. Kampf, A. J. Ashe III, *Org. Lett.* **2007**, *9*, 679 – 681.
[21] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842 – 3888.
[22] M. K. Cyranski, *Chem. Rev.* **2005**, *105*, 3773 – 3811.
[23] a) D. Feller, D. A. Dixon, *J. Phys. Chem. A* **2000**, *104*, 3048 – 3056; b) M. H. Matus, K. Anderson, D. M. Camaioni, S. T. Autrey, D. A. Dixon, *J. Phys. Chem. A* **2007**, *111*, 4411 – 4421.
[24] D. A. Hoic, W. M. Davis, G. C. Fu, *J. Am. Chem. Soc.* **1995**, *117*, 8480 – 8481.
[25] Crystallographic data for **7**: $C_7H_6BCrNO_3$; $M_r = 291.12$; crystal size $0.20 \times 0.14 \times 0.09$ mm; monoclinic; space group $P21/c$; $a = 11.5311(8)$, $b = 6.9443(5)$, $c = 12.2196(8)$ Å; $\beta = 115.946(1)°$; $V = 879.86(11)$ Å$^3$; $Z = 4$; $\rho_{calc} = 1.623$ g cm$^{-3}$; $\mu(Mo_{K\alpha}) = 1.267$ mm$^{-1}$; $F(000) = 432$; $\lambda = 0.71073$ Å; $T = 173(2)$ K; $2\Theta_{max} = 54.00°$; 9413 reflections measured [$R_{int} = 0.0262$];, 1915 reflections observed; 142 refined parameters; $R1 = 0.0293$, $wR2 = 0.0728$ for reflections with $I > 2\sigma(I)$; $R1 = 0.0345$, $wR2 = 0.0765$, and $GOF = 1.027$ for all data; max/min residual electron density $+0.439/-0.201$ e Å$^{-3}$. CCDC 709282 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[26] Y. Wang, K. Angermund, R. Goddard, C. Krüger, *J. Am. Chem. Soc.* **1987**, *109*, 587 – 589.