BN benzonitrile: an electron-deficient 1,2-dihydro-1,2-azaborine featuring linkage isomerism†

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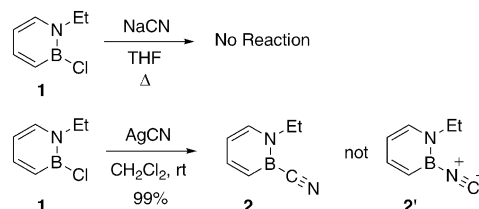**BN Benzonitrile 2, a 1,2-dihydro-1,2-azaborine bearing an electron-withdrawing boron substituent was prepared and characterized, and its coordination chemistry investigated; reactivity studies revealed that BN benzonitrile 2 undergoes BCN–BNC linkage isomerism upon coordination to Cr(CO)₅.**

1,2-Dihydro-1,2-azaborine is a six-membered aromatic heterocycle that is related to benzene by substitution of one of benzene's CC fragments with an isoelectronic BN unit.[1] Since the pioneering work by Dewar[2] and Ashe[3–5] on monocyclic 1,2-dihydro-1,2-azaborines (abbreviated as 1,2-azaborine), our research group has further explored the synthesis, structure, and reactivity of this heterocyclic structural motif,[6–9] which includes the isolation and characterization of the parent 1,2-dihydro-1,2-azaborine, a long-sought molecule that was believed to be too unstable to be isolated.[10]

In our continued efforts to create diversity of important aromatic structures through BN/CC isosterism, we recognized that 1,2-azaborines bearing electron-withdrawing boron substituents are still elusive. In particular, benzonitrile structures have attracted our attention because of their wide utility as biologically active agents.[11] In this communication, we describe the synthesis and characterization of a BCN-substituted 1,2-azaborine, and we demonstrate that the BCN bond undergoes linkage isomerism, a reactivity pattern that is distinct from the all-carbon system.
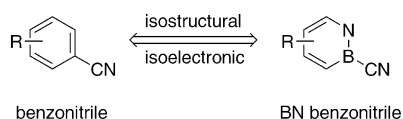
Benzonitriles are commonly synthesized from aryl halides *via* the Rosenmund-von Braun reaction using stoichiometric amounts of copper(ɪ) cyanide.[12] More recently, transition-metal-catalyzed methods for cyanation of aryl halides have been developed.[11] We previously synthesized 1,2-azaborine chloride **1** (Scheme 1), which can be regarded as a 1,2-azaborine-based aryl-halide equivalent.[6] The electrophilic

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Scheme 1 Synthesis of BN benzonitrile **2**.

character of boron in **1** permits the access to a wide range of *B*-substituted 1,2-azaborines *via* simple displacement of the chloride by a negatively charged nucleophile. We envisioned that NaCN could serve as a suitable nucleophile to yield the desired BN benzonitrile **2**. However, treatment of **1** with NaCN resulted in no reaction, even upon heating. After screening a variety of conditions, we determined that AgCN is a suitable coupling reagent with **1** to furnish BN benzonitrile **2** in quantitative yield (Scheme 1).
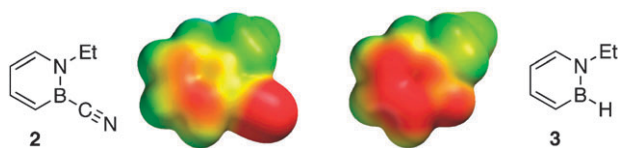
The cyanide anion is an ambident nucleophile,[13] and as such, it was unclear whether the product formed was BN benzonitrile **2** or BN benzoisonitrile **2′**. To determine the connectivity of **2**, we treated precursor **1** with labeled $Ag^{13}C^{15}N$. Isotopic enrichment permitted the observation of the nitrile carbon as a broad quartet (δ 126 ppm, q, $^1J_{BC}$ = 85 Hz) in the ^{13}C NMR spectrum due to coupling with the ^{11}B atom (S = 3/2). The ^{15}N NMR spectrum shows a sharp doublet ($^1J_{CN}$ = 15 Hz), consistent with coupling to the ^{13}C nucleus. IR spectra of **2** and **2'** were calculated at the DFT B3LYP/DZVPZ level (see Supplementary Information†). Whereas the calculated spectrum of **2′** shows a strong vibration for the $C{\equiv}N$ bond at 2190 cm^{-1}, the corresponding calculated vibration in **2** is extremely weak at 2300 cm^{-1}, providing another distinction between **2** and **2′**. The experimentally observed IR spectrum of **2** does not exhibit a peak in the expected stretching frequency of cyanides around 2200 cm^{-1}. Thus, the experimental NMR and IR data are consistent with the formation of **2**, not **2′**. The calculated relative zero-point energies (ZPE) of **2** and **2′** indicate that BN benzonitrile **2** is thermodynamically more stable than its isomer **2′** by 3.7 kcal mol^{-1}. Nucleus Independent Chemical Shift (NICS)[14] calculations suggest nitrile **2** (NICS(1) = −7.55) is slightly more aromatic than isonitrile **2′** (NICS(1) = –6.96).

To gain additional insight into the electronic structure of **2**, we calculated the electrostatic potential surface (ESP) of **2** and contrasted it with the ESP for the BH-substituted 1,2-azaborine **3**. Fig. 1 illustrates that in BN benzonitrile **2**, most of the negative charge (highlighted by the red color) is localized at the electron-withdrawing CN substituent. In contrast, the ESP map

Fig. 1 Electrostatic potential maps at the 0.002 electron/a.u.[3] density iso-contour level with an electrostatic potential range from −13.6 to 54.4 kcal mol^{−1} for 1,2-azaborines **2** and **3**. Blue is positive potential (repulsive for the positive charge), red is negative potential (attractive for the positive charge) and green represents near zero potential.

Table 1 ^{1}H and ^{13}C NMR shifts of *B*-substituted 1,2-azaborines

| Boron substituent	H$_{ortho}$	H$_{para}$	C$_{ortho}$	C$_{para}$
NMe$_2$	6.21	5.72	124	105.5
H	6.84	6.40	131	112.3
CN	6.99	6.64	131	115.1

Experimental chemical shift [ppm] in CD$_2$Cl$_2$.

of **3** indicates a greater localization of negative charge on the 1,2-azaborine ring.

NMR spectroscopy has also been applied to evaluate substituent effects on the π electron density of aromatic molecules.[15] In particular, studies by Herberich *et al.*[16] and Fu *et al.*[17] have shown that electron donation by boron-bound substituents in boratabenzenes, a family of boron-containing heterocycles that is isoelectronic to 1,2-azaborines, leads to upfield shifts of the *ortho* and *para* resonances in the ^{1}H and ^{13}C NMR spectra. The ^{1}H and ^{13}C NMR chemical shifts observed for BN benzonitrile **2** (Table 1) suggest that hetero-cycle **2** is an electron-deficient 1,2-azaborine.

Fig. 2 illustrates the calculated HOMO and LUMO of BN benzonitrile **2**. Similar to the parent 1,2-dihydro-1,2-azaborine,[10] the HOMO orbital coefficients are largest at the *ortho* (3) and *para* (5) positions of the heterocycle with additional π electron density mostly localized at the nitrogen atom of the cyano group. The LUMO of **2** shows a relatively large coefficient at boron consistent with boron's electrophilic nature. It is also worth noting that the LUMO is antibonding with respect to the CN p bond whereas the HOMO of **2** has bonding character.

We next explored the coordination behavior of BN benzo-nitrile **2**.[18] When **2** was treated with (MeCN)$_3$Cr(CO)$_3$ in THF at 60 °C, we observed evidence for the formation of the piano-stool complex **4** by ^{1}H and ^{11}B NMR as a minor component of a complex mixture (eqn (1)).[19] However, upon work-up we

were able to only isolate complex **5** as yellow crystals in low yield.

(1)
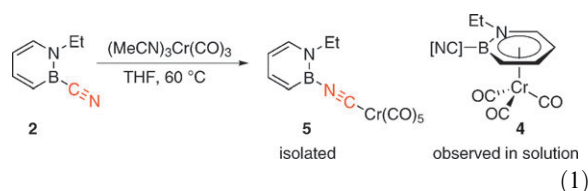
Crystals of **5** suitable for single-crystal X-ray analysis were grown from a saturated pentane solution. The X-ray structure of **5** revealed that the original BCN linkage in **2** underwent linkage isomerization under the reaction conditions (Fig. 3).[20–22] The structure is nearly co-linear through the B–N(2)–C(7)–Cr group (∠ B–N(2)–C(7) = 172.4(3)°, ∠ N(2)–C(7)–Cr = 179.3(3)°), indicating sp hybridization for both C(7) and N(2). The B–N(2) bond distance in **5** (1.489(4) Å) is comparable to the one in (CO)$_5$Cr(*CN*B(CH(SiMe$_3$)$_2$)$_2$) (B–N = 1.475(6) Å), which to the best of our knowledge, is the only other reported crystal structure of a trigonal-planar boron isonitrile complex.[23] The N(2)–C(7) bond distance (1.153(4) Å) in **5** is comparable to (CO)$_5$Cr(*CN*B(CH(SiMe$_3$)$_2$)$_2$)[23] (NC = 1.159(5) Å) and to reported (CO)$_5$Cr(*CN*Ar) structures (NC = 1.151(3) Å).[24] The C(7)–Cr bond length (1.981(3) Å) in **5** is also very similar to the ones exhibited by (CO)$_5$Cr(*CN*B(CH (SiMe$_3$)$_2$)$_2$)[23] (C–Cr = 1.971(4) Å) and (CO)$_5$Cr(*CN*Ar)[24] complexes (C–Cr = 1.968(3) Å). It is worth noting that electron-rich pentacarbonyl(isocyanide)-chromium(0) complexes show long NC–Cr distances (*e.g.*, 2.000(3) Å in [(CO)$_5$Cr(CN*NH*$_2$)]) whereas electron-withdrawing groups on the cyano moiety shorten the C–Cr distance (*e.g.*, 1.883(3) Å in [CO)$_5$Cr((CN*CN*)]).[23] The observed structural parameters are consistent with a strong contribution of the resonance form **A** relative to **B** in complex **5**.

We are interested in the effects of the electron-withdrawing NCCr(CO)$_5$ substituent on the intra-ring bond distances of the six-membered BN heterocycle. We determined that the intra-ring bond distances to boron in **5** are the shortest reported for a 1,2-azaborine (N(1)–B = 1.412(4) Å and B–C(3) = 1.486(5) Å), consistent with substantial positive charge at boron.

The low-yielding synthesis of **5** via eqn (1) posed a challenge for us to fully characterize complex **5**. Thus, we sought to independently synthesize **5** via alternative routes. Gratifyingly,
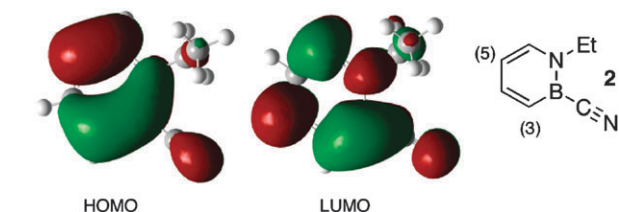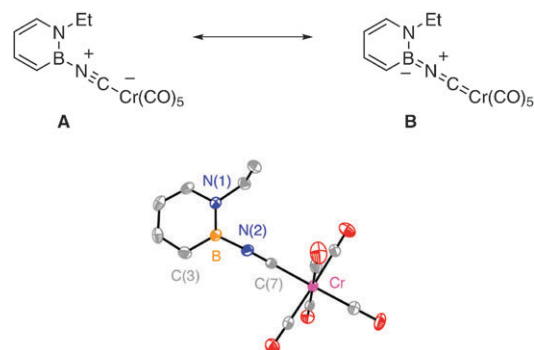
**Fig. 2** HOMO and LUMO of **2** calculated at the B3LYP/DGDVP2 level.

Fig. 3 ORTEP illustrations of **5**, with thermal ellipsoids drawn at the 35% probability level.

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we discovered that treatment of 1,2-azaborine precursor **1** with sodium pentacarbonylcyanochromate[25] furnished the desired adduct **5** in quantitative yield (eqn (2)).

$$\text{(2)}$$
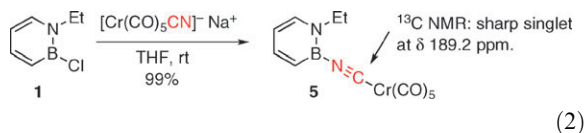
^{1}H and ^{11}B NMR spectra of the material obtained by eqn (2) were consistent with the previously prepared material *via* eqn (1). The ^{13}C NMR spectrum showed the isonitrile carbon as a sharp singlet at 189.2 ppm as well as two unique carbonyl groups, consistent with the *cis* (215.4 ppm) and *trans* (217.6 ppm) CO ligands. Finally, in the IR spectrum of **5**, the observed $C \equiv N$ stretching frequency at 2130 cm^{-1} is comparable to those observed in related $(CO)_5Cr(CNAr)$[24] complexes (2121 cm^{-1}) but is at a higher wavenumber than $(CO)_5Cr(CNB(CH(SiMe_3)_2)_2)$ (2113 cm^{-1}).[23] The $C \equiv O$ vibrations for **5** are at 2051, 1990, and 1954 cm^{-1}. These values are in good agreement with known $(CO)_5Cr(CNAr)$ complexes.[24] The experimentally determined IR spectrum of **5** is also in accord with its calculated spectrum (DFT B3LYP/DZVPZ level, see Supplementary Information†).

The mechanism for the formation of **5** in eqn (1) remains unclear. We hypothesize that reaction of **2** with $Cr(CO)_5(L)$ or $Cr(CO)_6$ present or generated in the reaction mixture could lead to **5**. To test this hypothesis, we reacted BN benzonitrile **2** with $Cr(CO)_6$ in THF at 60 °C and determined that **5** is generated in 23% yield (eqn (3)).

$$\text{(3)}$$
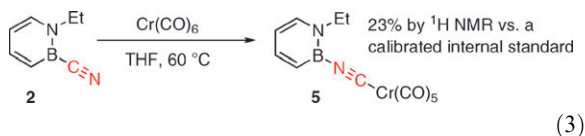
In summary, we synthesized and characterized BN benzonitrile **2**, which is the first 1,2-azaborine derivative bearing an electron-withdrawing boron substituent. This work continues to expand the synthetic toolbox for the generation of BN heterocycles related to biologically active structures. Reactivity studies reveal that the BCN bond in BN benzonitrile **2** undergoes linkage isomerism to furnish complex **5**. Crystallographic data of **5** establish that an electron-withdrawing boron substituent leads to shortening of the intra-ring BN and BC distances. Current efforts are geared toward developing a better understanding of the reactivity of the BCN functionality.

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