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PAPER

1,2-Nucleophilic addition of 2-(picolyl)organoboranes to nitrile, aldehyde, ketone, and amide†

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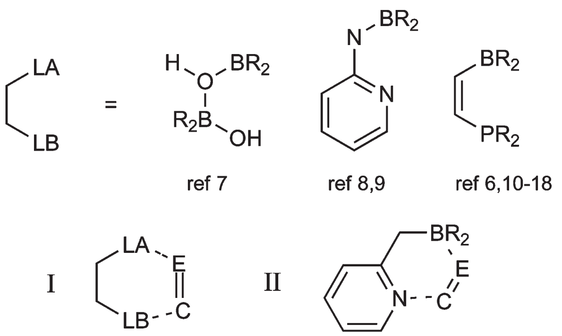
A series of 2-(picolyl)borane molecules were synthesized as products of the reaction between 2-(picolyl)-lithium and R_2BOMe (R = ethyl, 9-BBN, phenyl, 9-borafluorenyl). The 2-(picolyl)boranes were dimeric; whereas, monomers coordinated to LiOMe could be isolated when the synthesis was carried out in the presence of TMEDA and THF. The 2-(picolyl)boranes undergo reaction with nitriles, ketones, aldehydes, and amides with apparent 1,2-addition of the B–C(picolyl) bond to the unsaturated bond. Theoretical models reveal the presence of a donor orbital on the 2-(picolyl)borane with significant electron density at the benzylic carbon that we conclude was involved in nucleophilic attack on the electrophilic center of unsaturated organic functional groups.

Introduction

Frustrated Lewis pairs (FLPs) have received much attention recently. For instance, they have been shown to activate H_2, CO_2, RSSR, participate in hydrogenation and carboboration reactions, *etc.*[1,2] Theoretical investigation even points out the potential for heterolytic cleavage of the methane C–H bond in the presence of a highly preorganized active site.[3] Catalysis mediated by FLPs could offer new opportunities for catalyst design and optimization. An early example is the catalytic hydrolysis of 2-chloroalcohols in the presence of 8-quinoline boronic acid.[4]

Recently, Bourissou and co-workers reported the synthesis of 2-(picolyl)dicyclohexylborane, (2-(picolyl)BCy_2).[5] The molecule was found to exist in equilibrium between monomeric and dimeric forms. Addition of dichlororuthenium(II)cymene dimer to 2-(picolyl)BCy_2 led to dissociation of the dimer and formation of ruthenium–nitrogen and boron–chlorine dative bonds. No reactions with other substrates have been reported for 2-(picolyl)BCy_2. In particular, the preorganized nature of the monomeric FLP could allow their utilization as active site for activation of polar unsaturated organic molecules. Examples already exist in which a preorganized FLP forms a chelate structure (I) with polar unsaturated bond (Scheme 1).

A 1,2-borylphosphinoethene with bulky phosphine and highly electrophilic $–B(C_6F_5)_2$ group was found to undergo 1,2-addition to unsaturated substrates *trans*-cinnamic aldehyde and norbornene.[6] Interestingly, a similar bifunctional activation could be involved in the reaction of bis(pentafluorophenyl)borinic acid, $(C_6F_5)_2BOH$, with nitriles that led to six-member BOBOCN rings.[7] Reaction of 2-pyridylaminodiorganoborane with isocyanate led to a chelate structure in which the pyridine N-atom was donor to the isocyanate C-atom, and a boron–oxygen bond was formed that completed the six-member ring.[8,9] Balueva and co-workers reported 1,2-borylphosphinoethene reacted with small polar molecules such as ketene, diazo compounds,[10] ketenimine,[11] carbodiimide, isothiocyanate,[12] acetyl chloride,[13] aldehyde,[14,15] oxygen, carbon disulfide,[16] isocyanate,[17] thiocyanate,[18] sulfur and selenium;[19] though, it was unreactive toward nitriles and ketones.



Scheme 1 Activation of polar unsaturated organic molecules in the presence of preorganized FLP to form chelate structures (I), and starting model for interaction of 2-(picolyl)boranes with polar unsaturated bonds (II).

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† Electronic supplementary information (ESI) available: Experimental data for **1a**, **2a**, **2b** and reactions of **1**–**4** with ketones, aldehydes, amine, and nitriles, Ortep drawings, and Cartesian coordinates of atomic positions from DFT calculations. CCDC 871057–871077. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25518a

We synthesized a family of 2-(picolyl)boranes, 2-(picolyl)-BR_2 (R = Et, Ph; BR_2 = 9-borafluorenyl, 9-borabicyclononane (BBN)). The molecules were combined with several types of polar unsaturated molecules: nitriles, aldehydes, ketones, and amide. The 2-(picolyl)boranes do not form adducts with the polar unsaturated functional group with dual coordination (II, Scheme 1). Instead we observed the product of an apparent 1,2-nucleophilic addition (1,2-carboboration) of the 2-(picolyl)-borane to the unsaturated organic molecules (Scheme 2). Reactions with alkyl side-chains at the 2- or 6- position of a pyridine ring are well known due to the stabilization of the conjugated enaminate.[20–22] The additional boron atom enhances the stability of the enaminate. Therefore, the role of the 2-(picolyl)boranes as bifunctional catalysts in the activation of polar unsaturated bonds is diminished.

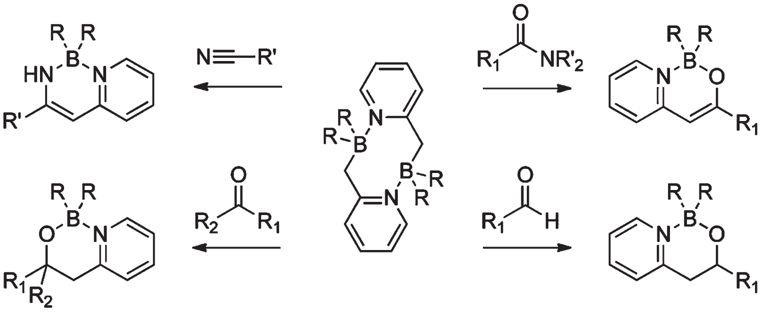
Results and discussion

The molecule 2-picoline was deprotonated in the presence of *n*-butyllithium, and addition of diorganomethoxyborane led to formation of 2-(picolyl)organoboranes **1–4** (Scheme 3). Isolation of the molecules required an additional step, as the initial crude product was the lithium methoxide adduct. Further treatment with BF_3OEt_2 or $B(OEt)_3$ produced $[2\text{-(picolyl)}BR_2]_2$ dimer without alkoxide. Alternatively, lithiation in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) followed by addition of the boron source led to clean formation of monomeric 2-(picolyl)borane as adduct with lithium methoxide.

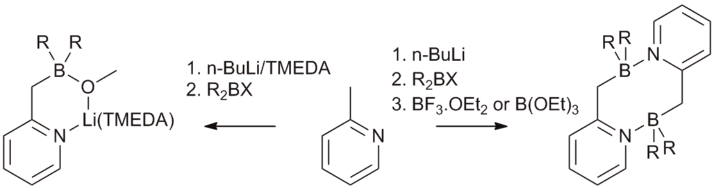
The structures of **1–4** were determined with X-ray crystallography (structural parameters can be found in the ESI†) and are shown in Fig. 1. In all cases the molecule is found in dimeric form wherein the central 8-member ring adopts a boat conformation (similar to the shape of cyclooctatetraene). Stereoisomerism is possible in the dimer structure, and the 8-membered ring can adopt non-superimposable clock-wise or counter clock-wise mirror images (Scheme 4). According to X-ray data, the isomerism in **1** and **3** was found to be opposite of **2** and **4**; however, we cannot so far rule out whether the four molecules could adopt either isomer. We note that boracycles (**2** and **4**) have opposite conformations than diorganoboryl with two free groups (**1** and **3**), and interestingly the 2-(picolyl)dicyclohexylborane dimer has like isomerism with **1** and **3**. The chair conformation has not been observed.

The boat shape 8-membered ring geometry is rigid in solution without flipping, as evidenced by NMR. Two well-separated doublets (**1**: 3.54 and 2.39 ppm) assigned to inequivalent benzylic protons were observed in the ^1H NMR spectrum. NOE experiments show the resonance at 3.54 ppm belongs to the inner ring proton and the resonance at 2.39 ppm to the outer ring proton. The rigidity of the dimer differentiates axial and equatorial ethyl groups (**1**), resulting in four different multiplets from each proton of ethyl CH_2 and two different triplets from ethyl CH_3. A sharp ^{11}B NMR peak at 0.77 ppm was found, and is within the chemical shift range for tetracoordinate boron. Negligible changes were seen in the ^1H and ^{11}B VT NMR spectra (in C_6D_6) up to 80 °C, suggesting that the rigidity of the boat shape 8-membered ring is retained even at elevated temperature and that there is no dissociation into monomer. NMR data of **1–4** show similar features: two different doublets from the benzylic protons and differentiated axial and equatorial diorganoborane groups. The dimers have different dihedral angles between the pyridine rings, depending on the group attached to boron: **1**, 64.02(4)°; **2**, 43.34(9)°; **3**, 89.22(5)°; **4**, 86.91(8)°. In contrast, 2-(picolyl)BCy_2 has a wide dihedral angle between the pyridine rings (113.05°). This dihedral angle may be symptomatic of the degree of sp^2 hybridization at the benzylic carbon and boron atoms.

A solution of **1** in acetonitrile was nearly colorless, but upon heating, the solution gradually turned deep yellow and finally



Scheme 2 Reaction products formed from 2-(picolyl)boranes and nitrile, amide, ketone, or aldehyde.



Scheme 3 Synthesis of 2-(picolyl)boranes **1** (R = Et), **2** (BR_2 = 9-BBN), **3** (R = Ph), **4** (BR_2 = 9-borafluorenyl).

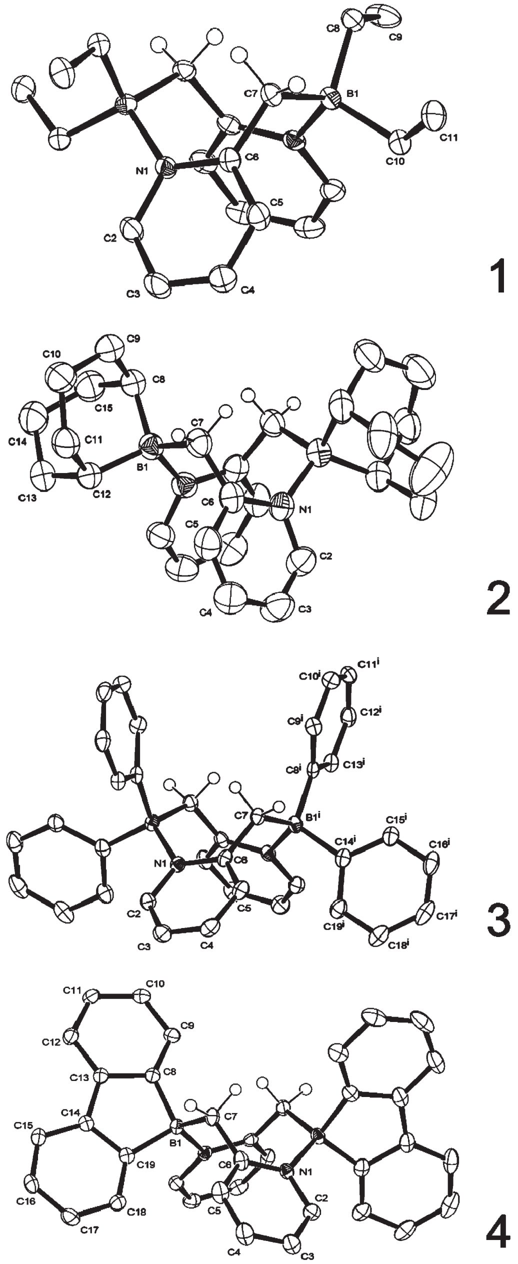
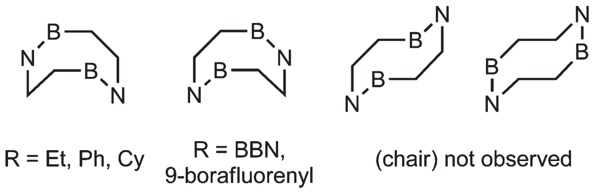


Fig. 1 Structures of **1–4** (descending from top to bottom) from single crystal X-ray diffraction data. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms except benzylic protons are omitted.



Scheme 4 Conformations and isomerism of the central 8-member ring of 2-(picolyl)borane dimers.

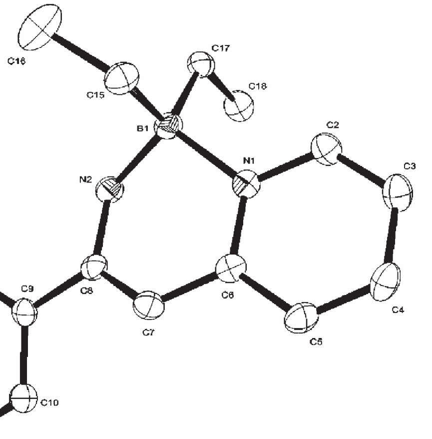


Fig. 2 Structure of **6** in the crystal. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted.

became orange. The ^{1}H NMR of the oily product after solvent removal indicated complete conversion to a new product, **5**. Two doublets from the benzylic protons of **1** disappeared and a broad peak at 3.85 ppm and a doublet at 4.42 ppm emerged. The oily nature of the product prevented it from structural characterization; however, the nature of the product was revealed by the reaction of **1** with benzonitrile, which produced orange–red crystals after recrystallization from CH_2Cl_2. Upon crystal structure determination a new product (**6**) was identified (Fig. 2) that apparently formed as a result of 1,2-addition of the B–C bond to the nitrile. The product was an aminoborane with intramolecular coordination of the pyridine nitrogen to form a 6-member ring. Due to the presence of a conjugated double bond in the ring, it is almost planar; whereas, boron is displaced from the plane. The ^{11}B NMR peak at 1.4 ppm is indicative of tetracoordinate boron.

Inspired by the nitrile insertion product, the reactivity of **1–4** with nitriles, aldehyde, ketone, and amide was also examined. The reactions were carried out in toluene with 1 : 2 stoichiometric ratio of dimer : unsaturated group (except acetonitrile and *N*,*N*-dimethylacetamide). Analogous 1,2-addition of the B–C (picolyl) bond to the unsaturated bond occurred, except that **4** proved unreactive. Reaction with dicyanobenzenes led to 1,2-addition with two equivalents of 2-(picolyl)borane. Aldehydes and ketones appeared to react more readily than nitriles. In contrast to the orange–red colored nitrile insertion products, the products from addition of aldehyde or ketone were nearly colorless due to the lack of conjugation in the new 6-member ring. The reaction of **1**, **2**, or **3** with *N*,*N*-dimethylacetamide gave rise to another type of product. The structure showed the insertion of the carbonyl group and absence of the dimethylamino group. As a result, the product has a conjugated 6-member ring in addition to the picoline ring, similar to the nitrile insertion product. The reactions with nitrile, ketone, aldehyde, and amide are summarized in Table 1 with experimental details in the ESI.†

The monomers, as LiOMe adducts, undergo reaction with nitriles in 1 : 1 stoichiometry to form a 1,2-insertion product identical to that formed from reaction of nitriles with dimeric species. The reaction of **1**-Li(OMe)(TMEDA), **1a**, with acetonitrile occurs at room temperature over about one hour; whereas, the reaction with dimeric **1** required elevated temperature. Compound **2** appears slightly less reactive than the monomeric LiOMe adducts.

Table 1 Reaction conditions and yields for products **5–24**

Borane	Electrophile	*T* (°C)	Time (h)	Isolated yield	Product
1	Acetonitrile	70	12	99	**5**
1a	Acetonitrile	25	1	100[a]	**5**
1	Benzonitrile	60	3	29	**6**
1	1,2-Dicyanobenzene	70	4	96	**7**
1	1,3-Dicyanobenzene	60	12	79	**8**
1	1,4-Dicyanobenzene	60	12	96	**9**
1	Benzophenone	60	3	76	**10**
1	2-Chloroacetophenone	80	12	47	**11**
1	4-Chlorobenzaldehyde	85	12	90	**12**
1	4-Nitrobenzaldehyde	80	1	51	**13**
1	*p*-Trifluorotolualdehyde	80	3	69	**14**
1a	*p*-Trifluorotolualdehyde	25	0.3	100[a]	**14**
1	Crotonaldehyde	70	3	100	**15**
1	Heptaldehyde	50	2	85	**16**
1	*N*,*N*-Dimethylacetamide	60	3	38	**17**
1a	*N*,*N*-Dimethylacetamide	25		dec.[a]	n/a
2b	Benzonitrile	50	3	44	**18**
2b	4-Chlorobenzaldehyde	25	12	81	**19**
2	*N*,*N*-Dimethylacetamide	60	2	94	**20**
3	Acetonitrile	100	12	98	**21**
3	Benzonitrile	100	3	72	**22**
3	4-Chlorobenzaldehyde	100	2	89	**23**
3	*N*,*N*-Dimethylacetamide	100	3	70	**24**
4	Benzonitrile	110	12	0	n/a

[a] NMR Yield.

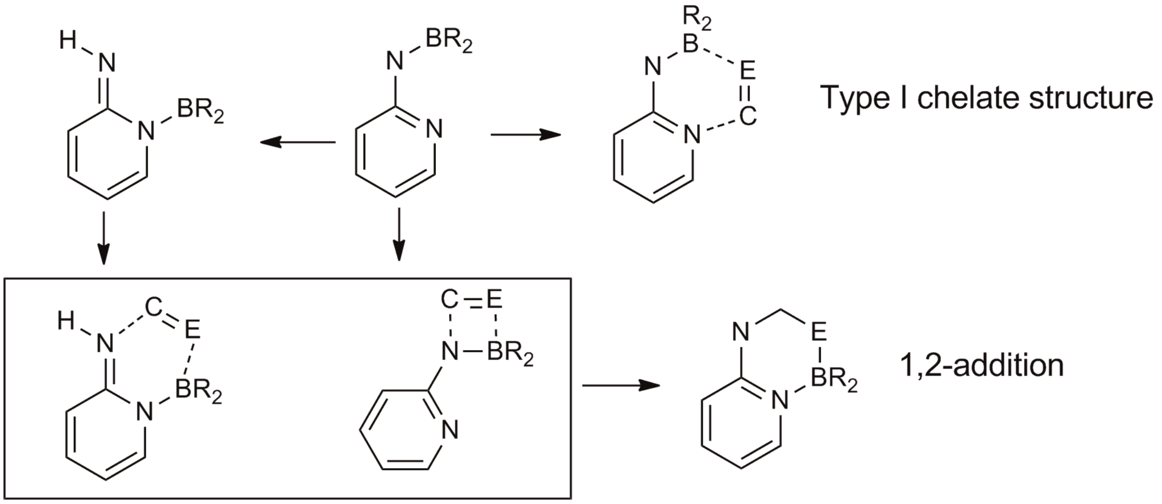
The reaction of 2-pyridylaminodiorganoborane (or 2-aminothiazoledialkylborane) with nitrile, carbonyl, or acetylene resulted in 1,2-addition of the B–N bond to the unsaturated bond.[23–25] This is in contrast to its reaction with isocyanate, which formed the chelated structures.[8,9] Theoretically, the 1,2-addition of the B–N bond to unsaturated bonds could proceed *via* 4-member or 6-member cyclic transition states. In the former, the 2° amine participates in S_N2 reaction with the electrophilic carbon of the substrate (nitrile, *etc.*); whereas, in the latter borotropic rearrangement to form a conjugated imine–aminoborane presents an imine nucleophile to the unsaturated substrate (Scheme 5). It is possible that the interaction of the 2° amine with the electrophile induces concerted weakening of the B–N bond that leads to a borotropic shift.

Neutral 2-pyridylaminoborane is isoelectronic with deprotonated (at the benzylic carbon) 2-(picolyl)borane, and suggests the mode of reactivity toward polar unsaturated bonds in the latter. Furthermore, Hamana and Sugasawa showed that addition of R_2B^+ (as triflate) to 2-picoline sufficiently stabilized the enaminate that it subsequently participated in nucleophilic addition to aldehydes.[21] Related to this, addition of chiral R_2B^+ to oxazoline stabilized azaenolates led to a stereochemically selective aldol reaction.[26] Carboranyldibutylborane was found to undergo 1,2-addition with nitrile and aldehyde in basic solvent.[27,28] Base coordination to boron led to polarization of the B–C(carboranyl) bond and subsequent nucleophilic addition was proposed to occur through a 4-member cyclic transition state.

We attempt to rationalize the observation of apparent 1,2-addition of the B–C bond of 2-(picolyl)boranes to polar unsaturated bonds in an explanation that incorporates all of the above findings (Scheme 6). Noting the stability of the 2-picolyl anion, 2-(picolyl)borane is simply a borylated form wherein boron could stabilize the adjacent resonance stabilized carbanion upon deprotonation (to form a structure isoelectronic with 2-pyridylaminodiorganoborane). Furthermore, a borotropic shift would lead to a reactive conjugated tetraene intermediate. The observation that acetylene reacts with 2-pyridylaminodiorganoborane even suggests a Diels–Alder type mechanism. However, the conjugated tetraene is a resonance form of the *N*-boronium stabilized 2-picolyl anion. We propose that dimeric 2-(picolyl)boranes are susceptible to B–C bond breaking within the 8-member core due to the dual donation of electron density from nitrogen to boron. We note the observation of 1,2-addition to carboranyldibutylborane was promoted by Lewis base, and conclude that the dimer is source of *N*-boronium stabilized 2-picolyl anion that could participate in 1,2-addition to polar unsaturated bonds *via* 6-member cyclic transition state.

Computational study

Dimeric compounds. The origin of reactivity of dimeric **1–4** toward polar unsaturated bonds in organic molecules can be understood upon inspection of their molecular orbitals. The orbital analysis of the dimeric species is important since the NMR data shows no evidence of monomeric species in solution at elevated temperatures. Therefore, we propose that dimeric species are reactants in the apparent 1,2-carboboration of polar unsaturated substrates. We performed DFT calculations using the B3LYP/6-31G* basis set. The optimized geometry of **1–4** is approximately C_2 in symmetry. The energies and orbital surfaces (HOMO − 9 through LUMO + 1) were calculated with isovalue of 0.032 e^- au^{-3}. Our analysis will focus on the filled MOs that have significant probability at the benzylic carbon, with attention



Scheme 5 Proposed (4- or 6-member) cyclic transition states on the approach of polar unsaturated bond to 2-pyridylaminodiorganoborane to form the 1,2-addition product *versus* type I chelate structure.

to the $C_{(\text{picoline})}$–$C_{(\text{benzylic})}$–B interactions. The LUMO of all dimers **1–4** is localized on the pyridine rings, and we conclude that the electron rich atom of the polar unsaturated substrate does not form a dative bond to boron initially. Furthermore, as we have no evidence to support dissociation of the dimer **1–4** to monomeric species, we do not conclude type I chelate structures are possible. Among the (HOMO through HOMO − 9) orbitals, three types of MOs are conserved in compounds **1–4** that will be called pic(π*)C(σ)B, pic(π)C(σ)B, and C(σ)B as shown in Scheme 7.

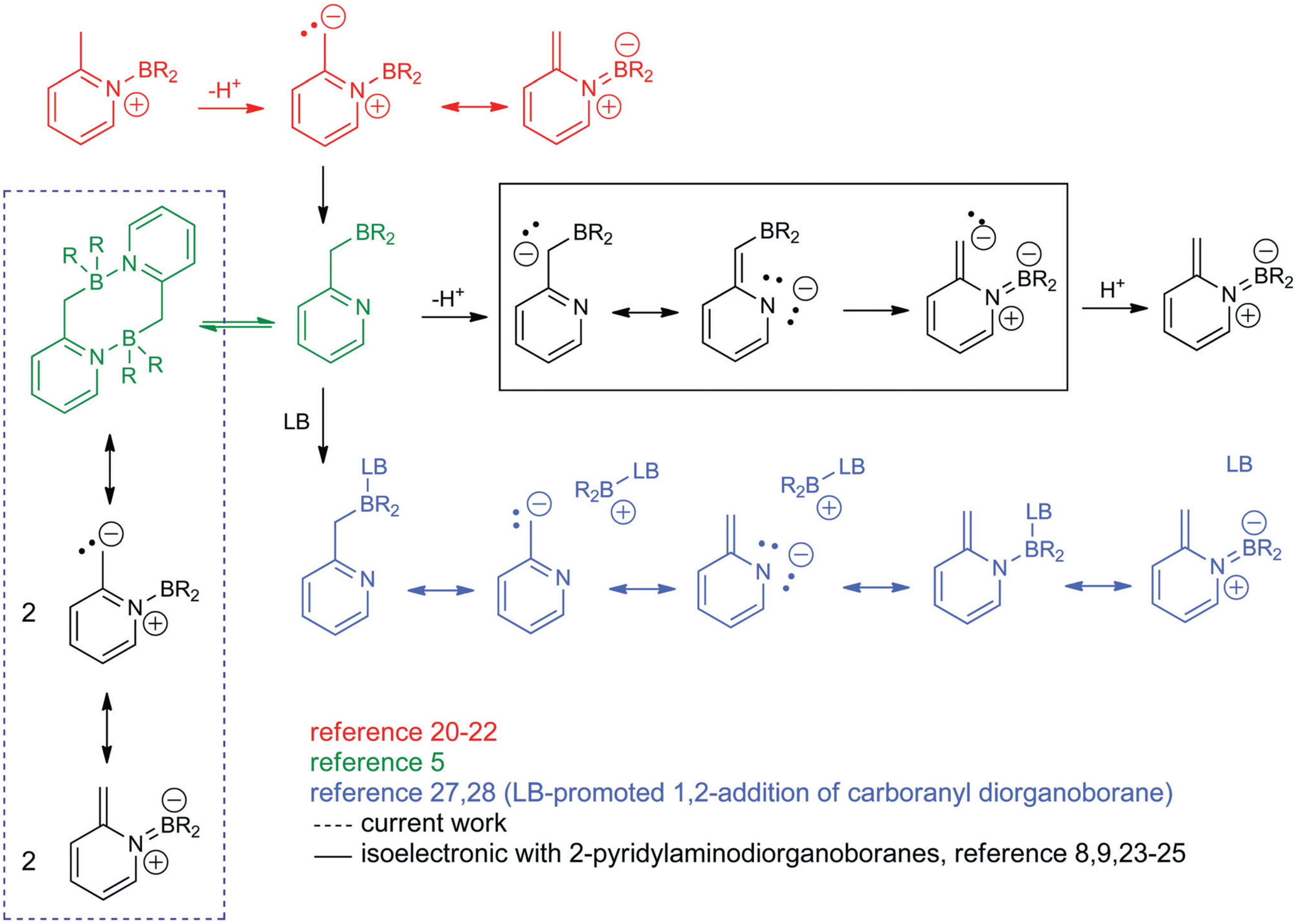
The orbital representations in Scheme 7 are only a simplified picture, as the complete wavefunctions have additional contributions throughout the molecule. The C(σ)B and pic(π)C(σ)B MOs are lower in energy than pic(π*)C(σ)B due to the stronger bonding interactions. The pic(π*)C(σ)B MO is antibonding between the picoline ring and the benzylic carbon and bonding between the benzylic carbon and boron. A loss of electron density from the MO would give rise to a weakening B–$C_{(\text{benzylic})}$ bond and more stable $C_{(\text{picoline})}$–$C_{(\text{benzylic})}$ bond.

The energies of (HOMO through HOMO − 9) were compared with attention to the pic(π*)C(σ)B type MOs (Chart 1). Molecules **3** and **4** include additional π-bonding MOs due to the presence of conjugated ring systems. While at first it may appear counter-intuitive that the energies of (HOMO through HOMO − 9) are increasing as the electron withdrawing power of the organic groups on boron is increasing, this can be understood given the additional π-bonding MOs that originate from phenyl and borafluorene groups. It is more instructive to view the trend of energy of a conserved MO type. Here, the attention will be focused on the pic(π*)C(σ)B type MOs because we propose these are the source of electron density that initiates the 1,2-nucleophilic addition reaction. In Fig. 3, the HOMO of **1** is shown, which is representative of the pic(π*)C(σ)B type MOs.

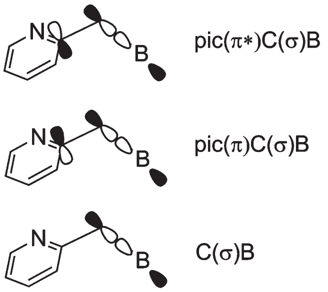
Interestingly, the energy of the pic(π*)C(σ)B type MO shows two consistent trends. First, as the electron withdrawing power of the organic groups attached to boron increases, the energy of the pic(π*)C(σ)B type MO decreases. Second, the (qualitative) rate of reaction is fastest with a higher energy pic(π*)C(σ)B type MO. Experiments show that **4** is extremely sluggish in reactions with polar unsaturated bonds; whereas **1** and **2** undergo the same reactions within hours or minutes.

The proposed mechanism of the reaction is that electron density from the benzylic carbon attacks an electrophilic carbon atom in a polar unsaturated bond in an S_N2 reaction. In this elementary step, a C–C bond forms due to donation of electron density from the pic(π*)C(σ)B type MO to the electrophilic carbon atom of a polar unsaturated bond. Donation of electron density from this orbital will lead to weakening of the B–C bond, which should be accompanied by charge buildup on the more electronegative member of the unsaturated bond. The newly concentrated electron density contributes to a bond-making step with boron. The result is the apparent 1,2-carboboration reaction of the B–$C_{(\text{benzylic})}$ bond to a polar unsaturated bond and formation of a 6-member ring.

Monomeric compounds as Li-base adducts. Faster reaction rates of 1,2-addition with polar unsaturated bonds were observed with monomeric counterparts. The molecules **1a**, **2a**, and **2b** (ESI†) have a high-lying HOMO that is mostly boron–oxygen (π*) in character; however, we do not observe products from nucleophilic addition of methoxide to electrophilic centers. The HOMO − 1 is a pic(π*)C(σ)B type MO deemed responsible for the 1,2-addition reaction. The calculated HOMO − 1 of **1a**, **2a**, and **2b** is higher in energy than the pic(π*)C(σ)B type MO in **1–4**. The same addition products were observed starting from **1** or **1a**, or from **2**, **2a**, or **2b**. We propose an identical reaction mechanism based on the MO analysis. The highest lying pic(π*)-C(σ)B type MO coincides with the fastest reactant in the 1,2-addition reaction. Whether the reactant is a 2-(picolyl)borane dimer or lithium methoxide adduct to the monomer, the molecules feature a reactive benzylic carbon with significant electron density in a high-lying frontier orbital. In both cases, the B–$C_{(\text{benzylic})}$ bond is activated by the presence of a base coordinated to boron. This type of activation was also observed in the polarization of B–$C_{(\text{carboranyl})}$ bonds that led to 1,2-addition to nitrile or aldehyde.[27,28]



Scheme 6 Formation of the *N*-boronium stabilized 2-picolyl anion upon dissociation of the 2-(picolyl)borane dimer *via* Lewis base induced dissociation of the B–C(benzylic) bond is the proposed route to the apparent 1,2-nucleophilic addition to polar unsaturated bonds.



Scheme 7 Frontier MOs of **1–4** with significant probability at the benzylic carbon.

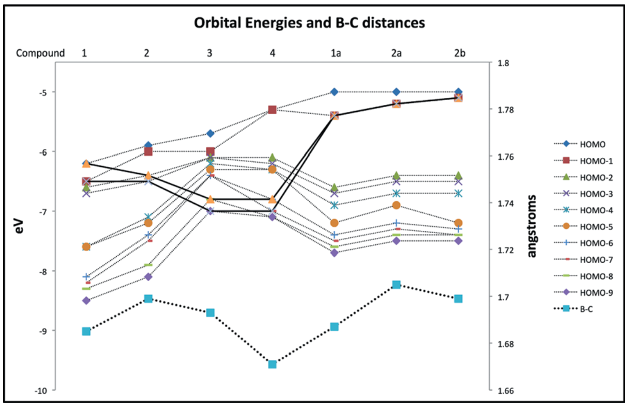


Chart 1 Calculated bonding orbital energies (HOMO through HOMO − 9) of compounds **1–4** are shown. In bold are the orbitals proposed to be involved in the first step of the 1,2-addition; S_N2 attack of the benzylic carbon to an electrophilic unsaturated carbon. The heavy dotted line marks the calculated boron–carbon bond distances in **1–4**.

Conclusion

Reaction of 2-(picolyl)lithium with R_2BX reagents led to 2-(picolyl)boranes. The molecules were found to be dimeric; however monomers coordinated to lithium alkoxide could be isolated. Members of the 2-(picolyl)boranes feature four-coordinate boron, and were found to undergo 1,2-nucleophilic addition (1,2-carboboration) to unsaturated bonds of nitrile, aldehyde, ketone, and amide. In theoretical models, a high-lying filled molecular orbital with significant electron density at the benzylic carbon was found and presumed responsible for the carboboration reaction. The orbital energy of the 2-(picolyl)borane

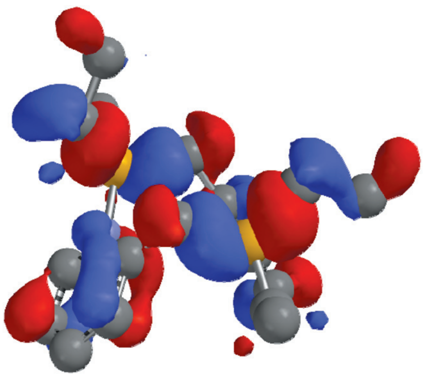


Fig. 3 Highest occupied molecular orbital (HOMO) of **1** from DFT calculation using B3LYP/6-31G* basis set.

nucleophile depends on the groups bound to boron and correlates qualitatively with the rate of reaction with unsaturated substrates. Similarly, the dimeric 2-(picolyl)borane can be viewed as source of *N*-boronium stabilized picolyl anion due to the destabilization of the B–C(benzylic) bond at the four-coordinate boron. A more detailed theoretical investigation into the specific reaction pathway may be an opportunity for future study. Potentially, as demonstrated in other studies, a chiral organoborane moiety could be substituted in order to create stereochemically selective reactions with aldehydes or asymmetric ketones, which may be a direction for future work.

Experimental section

General procedures

All procedures were carried out using standard Schlenk line technique or in a glovebox under N_2 or Ar atmosphere. 2-Picoline was distilled over CaH_2. THF, dichloromethane, acetonitrile, hexane and pentane were obtained from solvent dryer system (Puresolv). Diethylmethoxyborane, 9-methoxy-9-BBN (1.0 M in hexane), *n*-butyllithium (1.6 M in hexanes), benzonitrile, benzophenone and *N*,*N*-dimethylacetamide were purchased from Aldrich. Benzonitrile and *N*,*N*-dimethylacetamide was dried over 4 Å molecular sieve. Diphenylmethoxyborane[29] and 9-methoxy-9-borafluorene[30] were synthesized according to the literature. ^{1}H, ^{13}C and ^{11}B NMR spectra, VT NMR, as well as 2D-COSY, HMQC and 1D-NOE experiments, were obtained using Varian 200 MHz Mercury-plus NMR spectrometer or 400 MHz JEOL ECS-400 NMR spectrometer. Elemental analysis was carried out using an Exeter CE-440 Elemental Analyzer or performed by Atlantic Microlab, Inc. HRMS data were obtained using Bruker Daltonics ESI FTICR MS at the South Dakota State University Mass Spectrometry facility. Experimental data for **1a**, **2a**, **2b** and **5–24** can be found in the ESI.†

(2-Picolyl)diethylborane dimer (1)

2-Picoline (6.0 g, 64.4 mmol) was dissolved in 40 mL THF and cooled to −78 °C. To this 41.6 mL (66.6 mmol) of 1.6 M *n*-BuLi solution in hexane was added slowly and kept at −78 °C for 30 min. Diethylmethoxyborane (6.4 g, 64.0 mmol) in 20 mL THF was added *via* cannula. The contents were allowed to warm to room temperature overnight. Then the contents were again cooled to −78 °C and $BF_3{\cdot}OEt_2$ (9.1 g, 64.1 mmol) in 20 mL of THF was added *via* cannula. The solution was allowed to warm to room temperature overnight. The solvent was removed under vacuum, and an orange–brown oil remained in the flask. Purification was performed by acetonitrile–hexane extraction. The acetonitrile portion was dark, and the hexane portion was light orange color. The hexane portion was kept, and evaporation of the solvent *in vacuo* gave an orange oil that crystallized in a glovebox. Analytically pure product was obtained by extraction of the product with pentane. Large prism crystals (up to 1 cm) were obtained upon slow evaporation of pentane in the glovebox. Yield: 4.72 g (45%). Mp: 76–78 °C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.39–0.56 (1 H, m, CH_2CH_3, H8), 0.81 (3 H, t, *J* 7.2, CH_2CH_3, H11a–c), 0.88–1.11 (2 H, m, CH_2CH_3, H8 and H10), 1.15–1.33 (1 H, m, CH_2CH_3, H10), 1.31 (3 H, t, *J* 7.4, CH_2CH_3, H9a–c), 2.39 (1 H, d, *J* 11.4, H7$_{out}$), 3.54 (1 H, d, *J* 11.4, H7$_{in}$), 6.03 (1 H, dt, *J* 7.2 and 1.8, H3), 6.70 (1 H, dt, *J* 7.0 and 1.6, H4), 6.81 (1 H, td, *J* 7.0 and 1.2, H5), 7.74 (1 H, d, *J* 6.2, H2). δ_C (50 MHz; $CDCl_3$; $CHCl_3$) 9.6 (C11), 10.9 (C9), 13.2 (br, C8 and C10), 33.9 (br, C7), 117.8 (C3), 126.5 (C5), 136.9 (C4), 143.6 (C2), 169.6 (C6). δ_B (128 MHz; C_6D_6; BF_3OEt_2) 0.77. Found: C, 74.26; H, 10.16; N, 8.79. $C_{10}H_{16}BN$ requires C, 74.58; H, 10.01; N, 8.70%.

(2-Picolyl)borabicyclononane dimer (2)

2-Picoline (2.0 g, 21.5 mmol) was dissolved in 30 mL THF and cooled to −78 °C. To this solution *n*-BuLi (1.6 M in hexane, 14 mL, 22.4 mmol) was added *via* cannula and kept cold for 1 h after which 9-methoxy-9-BBN (1.0 M in hexane, 21 mL, 21.0 mmol) was added *via* cannula. The reaction was allowed to warm to room temperature overnight. Solvent was removed *in vacuo* and the product was dissolved in 20 mL of CH_2Cl_2. $BF_3{\cdot}OEt_2$ (3.0 g, 21.1 mmol) in 10 mL of THF was added *via* cannula. Solvent was removed *in vacuo* and the product was extracted with CH_2Cl_2. Crystals formed by slow evaporation of the solvent. The product could be further purified by extraction with toluene. Yield: 1.8 g (39%). Mp: 126–128 °C. δ_H (200 MHz; $CDCl_3$; $CHCl_3$): 0.90–1.14 (3 H, br m, BBN), 1.53–1.87 (10 H, br m, BBN), 2.34 (1 H, br s, BBN), 2.74 (1 H, d, *J* 11.4, H7$_{out}$), 3.24 (1 H, d, *J* 11.2, H7$_{in}$), 6.56 (1 H, dt, *J* 6.8 and 1.6, H3), 6.94 (1 H, d, *J* 8.2, H5), 7.35 (1 H, dt, *J* 7.6 and 1.6, H4), 7.63 (1 H, d, *J* 6.2, H2). δ_C (50 MHz; $CDCl_3$; $CHCl_3$) 22.8, 24.0, 30.8, 31.6, 34.8, 117.1(C3), 125.5(C5), 136.8(C4), 144.7 (C2), 171.7(C6). HRMS (ESI) *m*/*z* calcd for (**2** + H_3O^+) $C_{28}H_{43}B_2N_2O$: 445.356148, found: 445.35704.

(2-Picolyl)diphenylborane dimer (3)

2-Picoline (1.0 g, 10.7 mmol) was dissolved in 15 mL THF and cooled to −78 °C. To this solution *n*-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was added and kept cold for 30 min. Diphenylmethoxyborane (2.1 g, 10.7 mmol) in 10 mL THF was added *via* cannula, and the contents were allowed to warm to room temperature overnight. The solvent was removed *in vacuo* and the product was dissolved in 40 mL of dichloromethane. BF$_3$·OEt$_2$ (1.6 g, 11.0 mmol) was added *via* cannula. After 30 min, solvent was removed *in vacuo* and the product was washed with 95% ethanol until white product remained. The product was sonicated in distilled water and the remaining white powder was filtered and washed with ethanol. Yield: 1.0 g (36%). Mp: >300 °C. δ_H (200 MHz; CDCl$_3$; CH$_2$Cl$_2$): 2.39 (1 H, d, *J* 11.8, CH$_2$), 3.81 (1 H, d, *J* 12.0, CH$_2$), 6.56 (1 H, dd, *J* 7.7 and 1.1, H5), 6.78–6.82 (2 H, br m, *o*-H$_{eq}$), 6.97–7.04 (3 H, br m, H3 and *o*-H$_{ax}$), 7.12–7.25 (6 H, br m, H-m and H-p), 7.59 (1 H, dt, *J* 7.6 and 1.6, H4), 8.54 (1 H, d, *J* 6.4 and 1.4, H2). δ_C (50 MHz; CDCl$_3$; CDCl$_3$) 119.0 (C3), 125.1 (C-p), 125.3 (C-p), 126.9 (C-m), 127.4 (C-m), 130.8 (C5), 132.1 (*o*-C$_{ax}$), 134.2 (*o*-C$_{eq}$), 137.8 (C4), 147.4 (C2), 168.8 (C6). δ_B (64 MHz; CDCl$_3$; BF$_3$OEt$_2$) 2.45 (br). HRMS (ESI) *m*/*z* calcd for (**3**$^+$) C$_{36}$H$_{32}$B$_2$N$_2$: 514.275158, found: 514.27789. Found: C, 83.08; H, 6.34; N, 5.45. C$_{18}$H$_{16}$BN requires C, 84.08; H, 6.27; N, 5.45%.

9-(2-Picolyl)-9-borafluorene dimer (4)

2-Picoline (1.0 g, 10.7 mmol) was dissolved in 20 mL of THF and cooled to −78 °C. To this solution *n*-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was added and kept cold for 1 h. 9-Methoxy-9-borafluorene (2.0 g, 10.3 mmol) was dissolved in 20 mL of THF and added *via* cannula. The solution was allowed to warm to room temperature overnight and the solvent was removed *in vacuo*. The product was dissolved in 20 mL of dichloromethane and BF$_3$·OEt$_2$ (1.6 g, 11.0 mmol) was added. Solvent was removed *in vacuo* and the product was washed with cold acetonitrile until a light tan product was obtained. The product was dried in air and purified by extraction with dichloromethane. Colorless crystals formed upon solvent evaporation. Yield: 0.91 g (33%). Decomp. >200 °C. δ_H (200 MHz; CDCl$_3$; CH$_2$Cl$_2$): 2.33 (1 H, d, *J* 12.4, CH$_2$), 4.66 (1 H, d, *J* 12.6, CH$_2$), 6.83 (1 H, dt, *J* 6.7 and 1.5, H3), 6.99 (1 H, d, *J* 7.4, H18), 7.09 (1 H, dt, *J* 7.4 and 1.0, H10), 7.15–7.31 (3 H, m, H17, H5, H11), 7.38 (1 H, dt, *J* 7.4 and 1.4, C16), 7.64 (1 H, dt, *J* 7.6 and 1.6, C4), 7.75 (1 H, d, *J* 7.4, C12), 7.77 (1 H, d, *J* 7.0, C9), 7.84 (1 H, d, *J* 7.4, C15), 8.13 (1 H, dd, *J* 6.5 and 1.3, H2). δ_C (50 MHz; CDCl$_3$; CDCl$_3$) 37.6 (br, CH$_2$), 119.5 (C12), 120.1 (C15), 120.3 (C3), 126.9 (C17), 126.5 (C10), 126.9 (C16), 127.0 (C5), 129.5 (C11), 129.8 (C9), 130.9 (C18), 138.7 (C4), 145.6 (C2), 147.2 (C13/14), 148.3 (C13/14), 167.9 (C6). δ_B (64 MHz; CDCl$_3$; BF$_3$OEt$_2$) 2.45. HRMS (ESI) *m*/*z* calcd for (**4** + H$^+$) C$_{36}$H$_{29}$B$_2$N$_2$: 511.251683, found: 511.24775.

Computation

Theoretical models were computed using density functional theory with the B3LYP method and 6-31G* basis set using the Spartan'10 GUI/computational engine.[31] The ground state equilibrium geometry was calculated under vacuum. For each molecule, the molecular orbitals are shown at isovalue of 0.032 e$^-$ au^{-3}. The atomic connectivity within the model was established within the GUI, and the geometry was initially refined using MMFF molecular mechanics.

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