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Substituent Effects

Synergistic Effects of Lewis Bases and Substituents on the Electronic Structure and Reactivity of Boryl Radicals

Dongmei Lu,^{*,[a]} Chao Wu,^[b] and Pengfei Li^{*,[b]}

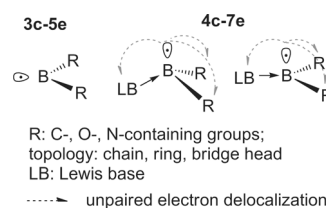
Abstract: Boryl radicals have the potential for the development of new molecular entities and for application in new radical reactions. However, the effects of the substituents and coordinating Lewis bases on the reactivity of boryl radicals are not fully understood. By using first-principles methods, we investigated the spin-density distribution and reactivity of a series of boryl radicals with various substituents and Lewis bases. The substituents, along with the Lewis bases, only affect the radical reactivity when an unpaired electron is in the boron p_z orbital, that is, for three-coordi-

nate radicals. We found evidence of synergistic effects between the substituents and the Lewis bases that can substantially broaden the tunability of the reactivity of the boryl radicals. Among Lewis bases, pyridine and imidazol-2-ylidene show a similar capacity for stabilization by delocalizing the spin density. Electron-donating substituents, such as nitrogen, more efficiently stabilize boryl radicals than oxygen and carbon atoms. The reactivity of a boryl radical is always boron based, irrespective of the spin density on boron.

Introduction

In contrast to carbon-, nitrogen-, and oxygen-centered radicals, boryl radicals have historically been much less explored. However, thanks to the rapid advances in boron chemistry and novel approaches to stabilizing these otherwise unstable species, methods for boryl-radical generation and their potential applications in organic synthesis and polymer chemistry have been greatly anticipated.^[1] Our interest is to map the relationship between the structure and reactivity of various boron-based reactive species, with an emphasis on those that may be harnessed in organic transformations. Herein, we report a computational study analyzing the reactivity of structurally representative boryl radicals.

If a boron atom covalently bonds to two groups and leaves one electron unused, a three-center five-electron (3c–5e) boryl radical is formed. The unpaired electron locates on the boron atom and protrudes out of the BR_2 plane (Scheme 1). Naturally, due to their substantial electron deficiency compared to a stable octet-electron configuration, 3c–5e radicals are highly reactive. Thus, by accepting a lone pair from a Lewis base (LB), they are transformed into more stable four-center seven-electron



Scheme 1. Boryl radicals interacting with substituents and Lewis bases.

tron (4c–7e) boryl radicals, which have been observed in experiments.^[1c,2] In addition to the partially alleviated electron deficiency, a 4c–7e boryl radical complex may be further stabilized by spreading the spin density onto the substituents and the coordinating Lewis base moiety through conjugation (hyperconjugation) effects. If the spin density is highly delocalized, the three-coordinate boron center assumes a trigonal-planar shape and the complex is called a π -type radical; otherwise, the boron is pyramidal and the complex is a σ -type radical (Scheme 1).^[1a,b,d]

Amine- and phosphine-bound boryl radicals were the first-generation boryl radicals (σ -type) that were intensively studied, by Roberts et al., in the 1980s and 1990s.^[1c,3] Some of the radicals have been used to accelerate hydrogen abstraction of electron-deficient C–H bonds by electrophilic alkoxyl radicals; this process is called polarity-reversal catalysis.^[1c] The catalytic efficiency depends on the stability of the associated boron radical, which further correlates to the B–H bond strength. The homolytic B–H bond dissociation energies (BDE) of amine and phosphine boranes, estimated by the Rablen group and later by the Zipse group by using density functional theory (DFT), were over 390 kJ mol^{-1} .^[4] Moreover, the substituents on the amine or phosphine groups did not have a significant effect on the BDEs.

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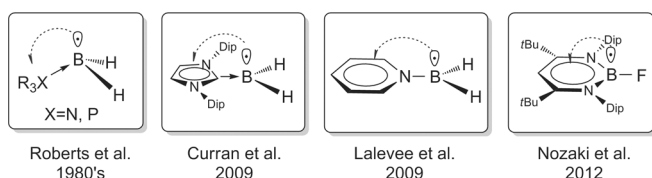
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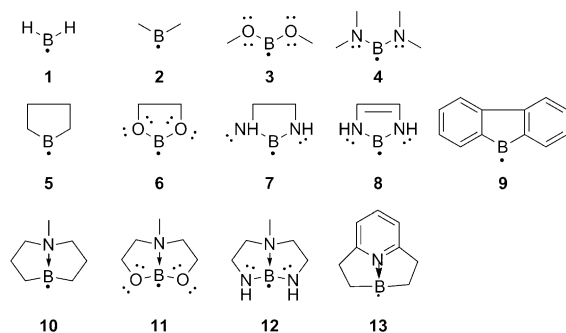


Scheme 2. Key boryl radicals developed in experiments.^[1c,2a–c] The dashed arrows indicate the direction of spin delocalization.

In 2009, a new generation of boryl radicals, containing N-heterocyclic carbenes as Lewis bases, were demonstrated by Curran et al.^[2a] to have higher stability (smaller BDE; Scheme 2). These boryl–N-heterocyclic carbene adducts are π -type radicals, resembling a benzyl radical.^[1b,d] Another possible approach for increasing the stability of boryl radicals might be to use common Lewis bases with a π -electron delocalizing backbone similar to N-heterocyclic carbenes. Thus, a series of pyridine derivatives were introduced by Lalevee et al.^[2b,f] to help stabilize boryl radicals. This approach was also predicted by the Zipse group in a slightly earlier theoretical investigation.^[4b] In 2011, in addition to modifying N-heterocyclic carbenes, Curran et al. studied the reactivity of boryl-radical/N-heterocyclic carbene complexes containing alkyl and aryl substituents on boron.^[2d] In parallel to the aforementioned Lewis base stabilizing strategy, the Nozaki group developed a novel B-heterocyclic radical in 2012 (Scheme 2); the unpaired electron is delocalized over a 1,3,2-diazaborinine framework, which is surrounded by bulky substituents. The structure was confirmed by single-crystal X-ray diffraction.^[2c]

Recent studies have, to some extent, highlighted the importance of the substituents, as well as the Lewis bases, in determining the properties of boryl radicals. However, how and to what degree substituents, especially heteroatom groups, which may be readily introduced onto boron and have shown important implications in other areas of boron chemistry, together with Lewis bases, affect the stability and reactivity of boryl radicals remains a key question. Herein, we attempt to address this in a systematic way by using computational tools.

Herein, we investigate thirteen boryl radicals that are representative of various potentially important boryl radicals (Scheme 3). Compound **1** is the parent radical. Compounds **2–4** are linear molecules with substituents containing carbon,



Scheme 3. Boryl radicals studied in this work. Lewis bases (LB): ammonia (NH₃), pyridine (py), and imidazol-2-ylidene (NHC).

oxygen, and nitrogen atoms, respectively. To make the discussion concise, only symmetric substitution patterns are considered. Compounds **5–9** represent similar functionalization to the previous group, but with a five-membered cyclic topology, which is also common in synthetic boron chemistry. In contrast to the saturated structures **5–7**, **8** and **9** have conjugated backbones linking the two substituents. Structures **1–9** are all 3c–5e boryl radicals, whereas **10–13** are 4c–7e radicals and each contains an intramolecularly coordinating Lewis base. This intramolecular coordination mode is analogous to that in boronates, which have found a wide range of applications in organic synthesis.^[5] For Lewis bases, three representative ones were chosen, including ammonia (NH₃), pyridine (py), and imidazol-2-ylidene (NHC). The structure, spin-density distribution, and interaction with Lewis bases of these boryl radicals, along with the corresponding boranes, are investigated by using density functional calculations.

Results and Discussion

Spin-density distribution of boryl radicals

Spin-density distribution is a basic property of a radical that has been found to be strongly correlated with the radical's stability and reactivity.^[4] For boryl radicals **1–13**, we first investigated how the spin-density distribution varies with molecular structure, before and after complexation with Lewis bases. The spin-density distribution is plotted for representative radicals (Figure 1).

For 3c–5e boryl radicals (**1–9**), the spin density is essentially located on the boron atom, as shown in both the isosurface plots and the spin-density populations (all above 0.90, see Table 1). The sp^2 boron center assumes a bent shape and the spin density is mainly in the third would be σ -bond direction. For 3c–5e radicals, neither heteroatoms (N and O) nor conjugated substituents significantly affect the spin-density distribution. For example, for a highly conjugated construct like the planar molecule **9**, the spin density still almost entirely resides on the boron atom (spin-density population = 0.95). This is readily understood by considering the minimum interaction between the in-plane singly-occupied molecular orbital on boron (SOMO, the shape of which is closely related to the spin-density distribution; Figure S1 in the Supporting Information) and the (nearly) orthogonal out-of-plane π orbitals on the two benzene rings.

However, by coordinating to a Lewis base, a $^{\bullet}BR_2$ radical's bent geometry transforms into a trigonal-planar or pyramidal structure (4c–7e), which causes an orientation switch of the unpaired electron from an in-plane orbital to a nearly perpendicular one. As a result, the spin distribution is now greatly affected by both the two substituents and the Lewis base. For instance, $1NH_3$ is a typical σ -type boron radical with a pyramidal geometry ($\angle NBH = 110.3^\circ$, $\angle HBN = 123.9^\circ$, $2\angle NBH + \angle HBN = 344.5^\circ$). All of the spin density is still on the boron atom, but it is switched to the p_z orbital orientation. By ligating to Lewis bases with a higher degree of conjugation, the spin density spreads over the adducts, as demonstrated in the $1py$

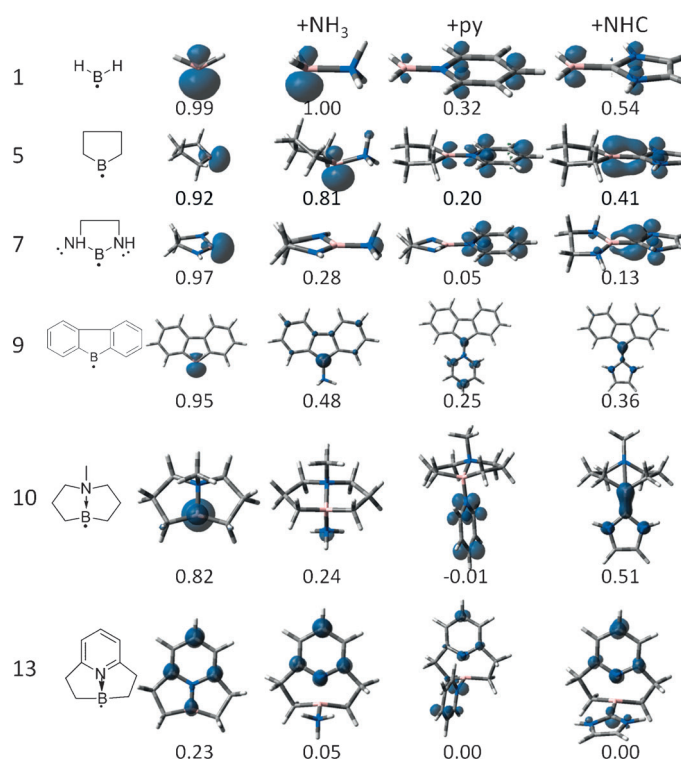


Figure 1. The spin density of selected boryl radicals and their adducts with Lewis bases (NH₃, py, and NHC). The NBO spin-density population for the boron atom is given below each structure. Hydrogen atoms are white, nitrogen atoms are blue, carbon atoms are gray, and boron atoms are pink. The spin-density isosurface is 0.01 a.u.

and 1NHC cases, generating planar π -type radicals. The spin-density population on boron is reduced from over 0.90 for **1** to 0.32 for 1py and 0.54 for 1NHC. Lewis bases like pyridine and NHC greatly help the spin density to delocalize. Notably, pyridine shows a stronger capability to cause delocalization for boryl radicals and NHC tends to keep the spin density near the B–C bond.

For most boryl radicals, the geometry of the boron center after complexing with pyridine and NHC is trigonal planar, whereas the remaining parts of the radical are essentially unaffected. A typical case is **5**, which is a twisted ring by itself with a dihedral angle of 38° between the four carbon atoms. After coordination by pyridine, the ring is twisted to 40°. The spin density is distributed over the planar part of the complex, that is, the pyridine ring plus the boron atom. Strong Lewis bases like pyridine and NHC dominate the spin-density distribution and the other two substituents are of secondary importance.

The geometry after NH₃ ligation is more complex, as the boron center can be either pyramidal or trigonal planar, which is the result of a synergistic effect (detailed in a later subsection) between the substituents and the Lewis base. Boryl radicals like **7** have two nitrogen-atom-based substituents, which are more π donating than carbon or oxygen atoms. As a result, these structures have a planar boron center with a low spin-density population. The spin-density populations on boron for these dinitrogen-substituted structures are 0.31 for

4NH₃, 0.28 for 7NH₃, and 0.26 for 8NH₃, which are much lower than for the dioxygen- (0.74 for 3NH₃ and 0.66 for 6NH₃) and dicarbon-substituted structures (0.80 for 2NH₃ and 0.81 for 5NH₃).

The 4c–7e boryl radicals **10–13** are already stabilized by intramolecular tertiary amine (**10–12**) or pyridine (**13**) groups. Although chemically **10–12** are similar to ammonia-stabilized radicals, their structures are nonplanar due to ring strain. As a result, the majority of the spin density remains on boron (details in Table 1), and is independent of the type of neighboring atoms. For example, compound **12**, the boron atom in which is sandwiched by two nitrogen atoms, has a spin-density population of 0.67, which is much higher than that of 4NH₃ and 7NH₃. Compound **13** has a flatter structure, and is chemically equivalent to a pyridine-stabilized radical, with much of its spin density delocalized onto the pyridine moiety. Adding one more Lewis base to these radicals is still possible, but it will weaken (or even break) the existing B–N dative bond. For instance, the B–N bond length in **13** is 1.42 Å and for 13NH₃, 13py, and 13NHC the bond length is elongated to 1.52–1.55 Å. The spin density redistributes and tends to shift to the stronger base. Moreover, constrained by boron's sp³ geometry, the second Lewis base can only be added in a nearly orthogonal direction to the first base.

In brief, 3c–5e-type boryl radicals (**1–9**) feature nearly all of the spin density on boron, and in contrast, their complexes with Lewis bases, including **10–13** (4c–7e type) usually have moderate to near-zero spin density on boron and a large portion of the spin delocalized on the Lewis base. Strong bases like pyridine and NHC always draw the spin density towards them and the substituents seem to play auxiliary roles in determining the distribution.














Reactivity of boryl radicals with Lewis bases and hydrogen atoms

The reactivity of boryl radicals generally depends on the specific reaction type, as well as the reaction environment. As most boryl radicals have been synthesized by homolytically breaking a B–H bond, the B–H bond strength (i.e., BDE) is commonly utilized to compare the reactivity between boryl radicals and hydrogen atoms. Herein, we first extend this idea to describe the reactivity between Lewis bases and boryl radicals, that is, we use the B–LB bond strength as the descriptor. Next, we will report the reactivity of boryl radicals with hydrogen atoms before and after the Lewis base stabilization. We use the binding energy to quantitatively describe the reactivity [Equation (1)], in which X = H, NH₃, py, or NHC, and B_{radical} is either unstabilized or Lewis base stabilized. BE_x includes the electronic energy and zero point energy; and the more exothermic (negative) the binding energy, the higher the reactivity.

$$BE_x = E(B_{\text{radical}}X) - E(B_{\text{radical}}) - E(X) \quad (1)$$

The binding energy between Lewis bases and boryl radicals (BE_{LB}) is ordered such that BE_{NHC} < BE_{py} < BE_{NH₃} (Figure 2, y axis), with a decreasing sequence of B–LB bond strengths. BE_{LB} does

Table 1. Binding energies [kJ mol⁻¹] of boryl radicals with Lewis bases and hydrogen atoms.

		Bd ^[a]	B-H ^[b]	B-NH ₃	Bd	B-NH ₃ -H ⁺	B-py	Bd	B-py-H ⁺	B-NHC	Bd	B-NHC-H ⁺
1		0.99	-418.4	-135.8	1.00	-402.3	-274.9	0.32	-278.0	-343.4	0.54	-304.2
2		0.91	-407.4	-85.3	0.80	-388.0	-227.0	0.21	-250.0	-281.7	0.40	-277.7
3		0.90	-414.7	-16.6	0.74	-397.4	-161.5	0.06	-257.3	-195.1	0.18	-294.7
4		0.91	-413.8	-16.3	0.31	-359.6	-172.3	0.05	-214.1	-198.5	0.17	-255.5
5		0.92	-418.4	-88.5	0.81	-389.9	-243.4	0.20	-238.4	-294.3	0.41	-276.2
6		0.93	-432.1	-49.6	0.66	-387.7	-216.8	0.08	-225.5	-248.9	0.20	-250.9
7		0.97	-430.8	-46.2	0.28	break ^[c]	-198.8	0.05	-203.0	-220.6	0.13	-245.2
8		1.01	-437.1	-43.4	0.26	break	-193.7	0.03	break	-218.0	0.07	-231.9
9		0.95	-424.8	-165.6	0.48	-342.1	-254.5	0.25	-263.3	-339.7	0.36	-271.7
10		0.82	-376.1	-9.6	0.24	n/a ^[d]	-81.0	-0.01	n/a	-169.1	0.41	n/a
11		0.74	-387.6	-24.3	0.16	n/a	-105.7	0.00	n/a	-253.7	0.25	n/a
12		0.67	-360.4	-37.9	0.37	n/a	-78.7	0.00	n/a	-237.6	0.16	n/a
13		0.23	-284.4	-15.4	0.05	n/a	-52.1	0.00	n/a	-90.6	0.00	n/a

[a] Bd: NBO spin density on boron atom in the structure of the left neighboring column. [b] B-X: binding energy of boryl radical and X (X = H⁺, NH₃, py, NHC; boryl radical can be 1 to 13 or Lewis base stabilized ones). [c] Molecular complex breaks off after optimization. [d] The interaction does not exist, so no binding energy is available.

not linearly correlate with boron natural bond orbital (NBO) spin density before ligation. BE_{LB} also does not show evidence of a linear correlation with the charge (Figure S2 in the Supporting Information). Lewis base stabilized radicals 10–13 weakly bond with a second Lewis base. A narrow distribution of the boron spin density in 1–9, featuring scattered BE_{LB}, spreads over a range of 180 kJ mol⁻¹ for weak bases like NH₃ and over a wider range (> 250 kJ mol⁻¹) for stronger bases like NHC (Figure 2).

atom (BE_H) is an important factor for describing the radical's reactivity.^[2b,f,4] Agreeing with the previous research by Rablen^[4a] on simple Lewis bases such as OH₂ and NH₃, we found good linear correlations between the spin density on boron and BE_H for radicals stabilized by various Lewis bases (Figure 3), which indicates that pairing of the unpaired electrons drives the radical–radical reaction.

Sometimes this hydrogen binding can replace the Lewis base, by forming a stable final structure. For example, 8NH₃–H

The above observation reaffirms that B–LB coordination is conceptually not a straightforward process like a radical–radical termination reaction. Intuitively, two elementary steps can be proposed to help understand the B–LB interaction: 1) An electron pair is donated from the Lewis base, which forces the unpaired electron of the boryl radical to switch into the p_z orbital, and 2) the unpaired electron can then interact with π and σ orbitals on other groups or atoms to redistribute the spin density. As a result, neither the spin density nor the charge on the boron prior to complexation can be directly correlated to the strength of the coordination. Moreover, it is easily deduced that the binding energy between Lewis bases and boryl radicals and the binding energy between the Lewis base stabilized boryl radicals and hydrogen atoms do not linearly correlate, as they are very different processes by nature, which is confirmed by our (Figures S2 and S3 in the Supporting Information) and others' studies.^[4]

The binding energy between a boryl radical and a hydrogen

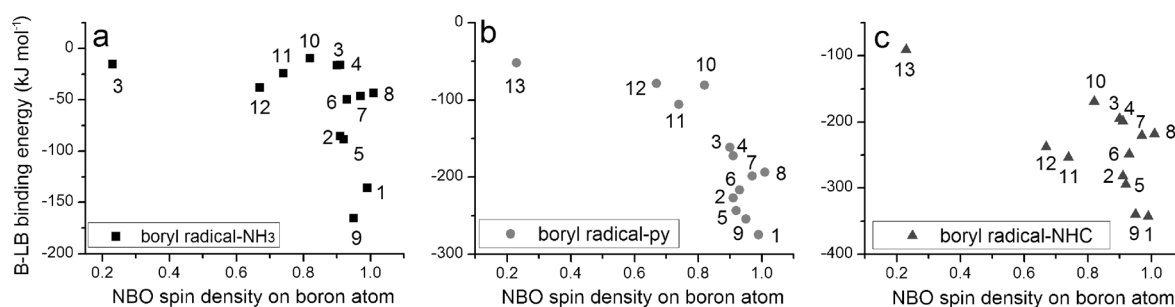


Figure 2. Plots of the spin-density population on the boron atom before reaction with the Lewis base versus the B–LB binding energy of 1–13 to a) NH₃, b) pyridine, and c) NHC.

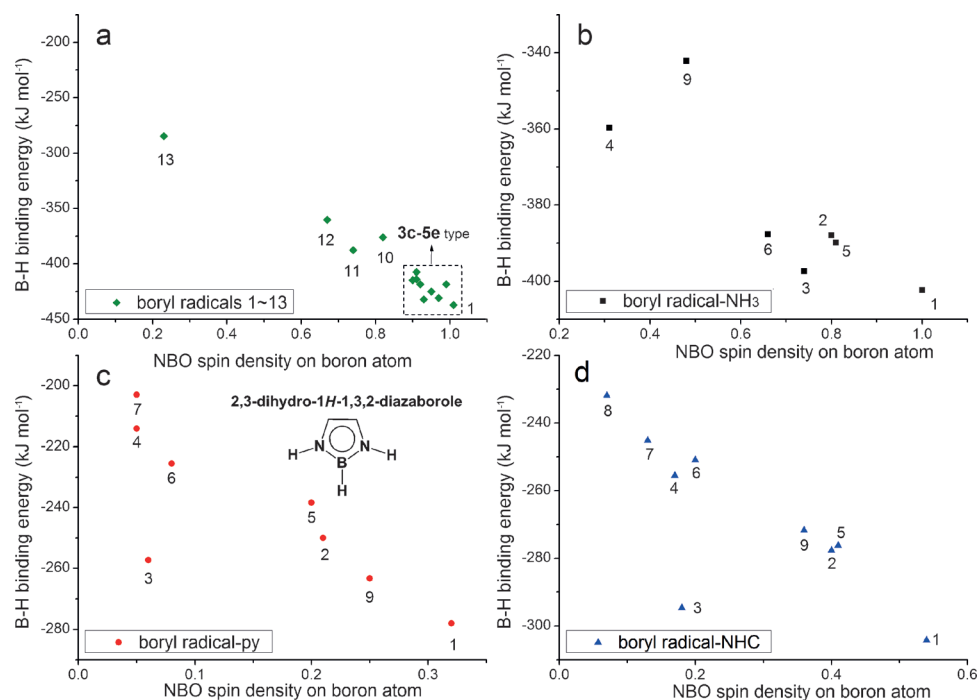


Figure 3. The correlation between the spin-density population on the boron atom before reaction and the B–H binding energy: a) 1–13, b) NH_3 -coordinated, c) py-coordinated, and d) NHC-coordinated boryl radicals. Fewer than nine points in b and c is due to omitted broken structures ($8\text{NH}_3\text{-H}$ and $7\text{NH}_3\text{-H}$ in b and 8py-H in c).

and 8py-H are missing in Figure 3b and 3c. As the bases fall off the complex, **8** is actually transformed into 2,3-dihydro-1H-1,3,2-diazaborole, a stable known compound showing characteristics of a heteroarene (Figure 3c, inset).^[6] For stronger bases like NHC, this transformation does not happen and for weaker bases like NH_3 , $7\text{NH}_3\text{-H}$ breaks off the NH_3 part to form 1,3,2-diazaborolidine.

Internally Lewis base coordinated boryl radicals **10–13** are less reactive in terms of the B–H bond strength than the 3c–5e-type radicals (Figure 3a, **1–9** enclosed by a dashed black rectangle). Again, it is evident that the BE_H 's of **10–12** (Figure 3a) are in the BE_H range of B– NH_3 radicals (Figure 3b) and the BE_H of **13** (Figure 3a) is in the B–py regime (Figure 3c), as they are actually stabilized by intramolecular tertiary amine and pyridine, respectively. Nevertheless, **13** has the weakest reactivity with Lewis bases among the four 4c–7e radicals (Figure 3a). The reason for this behavior is that **13** is near planar with the conjugation already extended to the boron atom, which makes it less reactive towards forming a tetrahedral boron center than nonconjugated and nonplanar structures like **10–12**. Only 3c–5e radicals can complex with a Lewis base and then react with a hydrogen atom, and thus fewer points are plotted in Figure 3b, 3c, and 3d. Overall, the B(LB)–H binding energy is proportional to the degree of spin localization on boron and follows the order $\text{BE}_\text{H} < \text{BE}(\text{B-NH}_3)_\text{H} < \text{BE}(\text{B-NHC})_\text{H} < \text{BE}(\text{B-py})_\text{H}$. The higher BE_H implies less reactivity and more stable boryl radicals.

Comparison between pyridine and NHC

NHC and pyridine are both Lewis bases featuring conjugated structures that interact with boryl radicals by making a π -type boryl radical. In the above analysis, NHC- and pyridine-coordinated boryl radicals show quantitatively similar reactivity with hydrogen atoms (Figure 3c and 3d), despite their clear difference in spin-density distribution (Figure 1). Since NHC and pyridine derivatives have been used in stabilizing boryl radicals under experimental settings,^[2b,f,4b] a comparison of the two Lewis bases would provide useful information for understanding and selecting Lewis bases for the future development of boryl radicals.

Several differences between the two bases are worth noting. The NHC's five-membered ring is

smaller than the six-membered py ring, which lessens the steric interaction with boryl radicals. This notion may be exemplified by **9**. Compound **9py** has a dihedral angle of 24° between **9**'s plane and the pyridine plane, but **9NHC** is entirely planar. When the two nitrogen atoms of the NHC have methyl substituents, there is some steric effect, and **9NHC(Me)** has a dihedral of 44° between **9**'s plane and the NHC ring plane, similar to that of **9py** (Supporting Information, optimization archive files, structure **9** + $\text{NHC}(\text{Me})$). The B–NHC interaction can be so strong that the original intramolecular stabilizing B–N bond sometimes cleaves. Notice the abnormally low BE_LB values of **11NHC** and **12NHC** in Figure 2c compared to those in Figure 2a and 2b. Actually, medium-sized rings are formed after the original intramolecular B–N bond breaks in both complexes (Figure S5a, inset, in the Supporting Information).

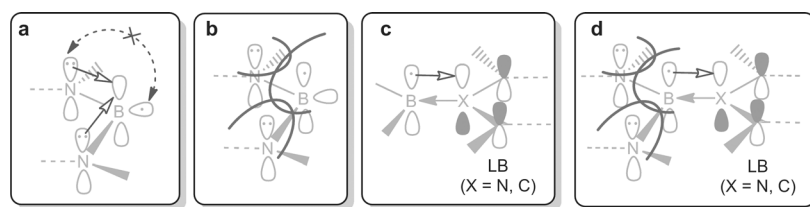
Lewis bases like NHC or pyridine can help lower the spin density on boron, which leads to weaker binding to hydrogen atoms by about 100 kJ mol^{-1} . With the help of substituents, the B–H bond strength can be further weakened by 80 kJ mol^{-1} (the BE range in Figure 3c and 3d). Particularly for pyridine complexes, the spin density is virtually zero for the electron-donating-atom substituted 3c–5e and all 4c–7e boryl radicals (Table 1), and thus pyridine-stabilized boryl radicals tend to form the weakest B–H bonds. Intramolecular Lewis base stabilized structures (**10–13**) form stronger B–H bonds than those of a few intermolecular Lewis base stabilized boryl radicals (Figure 3a, 3c, and 3d), implying that, probably due to ring strain, they are not the best choice for lowering reactivity towards radical–radical annihilation. The cyclic diarylboryl radical **9** is also not a top candidate, although substituents with

neighboring nitrogen atoms, either in linear form (**4**) or in a ring structure (**7**), are more promising for the formation of stable boryl radicals.

In short, there is no essential difference between pyridine and NHC in these compounds, as they are both good σ -donating and π -accepting Lewis bases. Other conjugated Lewis bases may have similar effects on stabilizing boryl radicals. Moreover, both pyridine and NHC here are in their parent forms and may be fine tuned by substituents on the conjugated rings.

Synergistic effect of substituents and Lewis bases

Herein, we illustrate the synergistic effects of substituents and Lewis bases in Scheme 4. Two models representing 3c–5e-type boryl radicals with only two substituents are depicted in Scheme 4a and 4b, in which nitrogen-containing substituents are used to exemplify the electron-donating groups. The



Scheme 4. Substituent, Lewis base, and synergistic effects in boryl radicals.

boron p_z orbital and the nitrogen p_z orbitals can form bonding orbitals by delocalizing the nitrogen lone-pair electrons (the blue arrows in Scheme 4), but the in-plane nonbonding boron orbital holding the unpaired electron cannot form molecular orbitals with the nitrogen p_z orbitals due to their orthogonal orbital symmetries (the crossed dashed arrow). Indeed, NBO analysis of **7** reveals that in terms of the traditional Lewis-type structure, which is the first-order approximation of the electronic structure of a molecule, one of the two nitrogen atoms (labeled N_1 and N_2) and boron form a double bond (for example, $B=N_1$). Moreover, the Lewis structure is further stabilized by secondary donor–acceptor interactions between bonds (lone pairs) and antibonds. The largest secondary stabilizing interaction is the electron donating from the other nitrogen atom (N_2 , ≈ 0.1 e of the lone pair electrons) to the $B-N_1$ antibonding π orbital, which has the highest second-order perturbative energy. All of these do not involve the unpaired boron electron, which is in the $sp^{1.25}$ NBO orbital. If the unpaired electron were in the p_z orbital of boron, as shown in Scheme 4b, then it would be unstable due to the electronic repulsion (“push”) from the nitrogen lone pairs. Rather than staying in the p_z orbital, the unpaired electron would return to the in-plane orientation, even when the sp^2 -type orbital has been occupied (see **7**NH₃ in Figure 1, in which the spin density of **7**NH₃ mainly resides on the NH₃). Thus, 3c–5e-type boryl radicals cannot be effectively stabilized by the substituents.

Scheme 4c illustrates a different scenario, the unsubstituted boryl radical is transformed into a 4c–7e-type structure by a li-

gating Lewis base and the unpaired electron is now forced to reside in the boron p_z orbital. If the Lewis base is a good π acceptor, such as an NHC or pyridine, the unpaired electron can be delocalized from the boron p_z orbital into the lowest unoccupied molecular orbital (LUMO) of the Lewis base and the radical assumes a flat geometry. If the Lewis base is a poor π acceptor, like NH₃, the 4c–7e radical will be pyramidal, as significant spin density remains on boron. Depending solely on the attraction (“pull”) of the LUMO of the Lewis base, a notable spin density always remains on boron, even for strong π -acceptor bases, such as in the cases of **1**py/NHC and **5**py/NHC (Figure 1).

Finally, the combination of substituents and Lewis bases can exert synergistic effects on the stability of boryl radicals (Scheme 4d). Complexation of a Lewis base to a 3c–5e boryl radical leads to two results: 1) the unpaired electron is in the boron vertical p_z orbital, and 2) both the substituents and the Lewis base can now interact more effectively with the unpaired electron. The p – π orbitals of boron, substituents, and the Lewis base collectively form a delocalized SOMO, which provides more room for spatial distribution of spin density. In addition, electronic characteristics of electron-donating substituents and a π -accepting Lewis base jointly invoke a “push–pull” electronic effect. If designed properly, they can cooperatively adjust the spin-density distribution, greatly altering the reactivity of boryl radicals.

This synergistic effect is clearly illustrated by the spin-density plots shown in Figure 1. For example, in 3c–5e-type radicals, **5** and **7** have similar spin densities on boron (0.92 and 0.97), irrespective of the nitrogen-containing substituents in **7**. By complexing to different Lewis bases, the difference in boron spin density is enlarged from 0.05 for the initial 3c–5e pair (**5** vs. **7**) to 0.15 for pyridine complexation, 0.28 for NHC complexation, and 0.53 for NH₃ complexation. For the unsubstituted case **5**, the Lewis base lowers the spin density on boron from 0.92 for **5** to 0.20 for **5**py, a large, but still limited reduction. In comparison, along with the electron-donating substituents in **7**, the spin density on boron is reduced to virtually zero for **7**py. A much wider tunability window of radical reactivity is achieved only if the Lewis base and the two substituents function synergistically.

Moreover, from Figure 3a, one can see that boryl radicals of 3c–5e configuration (the black rectangle enclosed points) extend only to a small B–H binding energy window of about 40 kJ mol^{−1}, in comparison with the 4c–7e values, which spread over a range of about 80 kJ mol^{−1} for any group of the three (NH₃, py, and NHC) Lewis base stabilized boryl radicals. These results once more suggest that, for Lewis base free boryl radicals, substituents alone provide limited room for modification and thus limited stabilization of these reactive species. In conjunction with Lewis bases, however, substituents do in gen-

eral demonstrate a powerful strategy for modification of the reactivity of boryl radicals.

Looking for “true” boryl radicals?

A number of researchers have discussed the degree to which the characteristics of boron remain in Lewis base stabilized boryl radicals.^[2a,c,f,4b] In our radical pool, 3c–5e radicals have over 90% boron character, but are unlikely to exist as reaction intermediates due to their high electron deficiency. The 4c–7e radicals coordinated with weak Lewis bases, such as NH₃, show appreciable characteristics of boron even when the substituents are electron donating, such as an amine group (the spin-density population on boron is always >0.15). B–py and B–NHC 4c–7e radicals delocalize the spin density to a greater degree. Specifically, pyridine-coordinated boryl radicals have the minimum spin-density population on boron. Pyridine- and NHC-stabilized boryl radicals are likely to be more stable, yet these compounds lost their boron character as a radical.

Although the stability and boryl characteristics counteract each other, their reactivity is still boryl based because the boron center can react strongly with a hydrogen atom (< –200 kJ mol^{–1}) despite the low spin density. The radical must react at the boron atom, since other atoms are already in their saturated or stable electronic configuration. Thus, as a chemical species, a boryl radical may have little boron character, but as a reactant, its reactivity is always boryl based.

Conclusion

We have systematically studied the synergistic effects of substituents and Lewis bases on the electronic structure and the reactivity of boryl radicals and the main conclusions are given below.

Synergistic effects

Two-coordinate three-center five-electron (3c–5e) boryl radicals show a trigonal-planar structure and the unpaired electron is in the plane and (nearly) orthogonal to p– π or σ orbitals on other parts of the molecule, leading to minimal interactions. By adding a Lewis base to form four-center seven-electron (4c–7e) radicals, the unpaired electron is pushed into a p_z orbital, allowing for stronger interactions with other components of the molecule. The weaker influences, on the reactivity of boryl radicals, coming solely from either substituents or Lewis bases can be magnified through their cooperative interactions, which has been verified by both the spin-density plots (Figure 1) and the doubling of the B–H binding energy range from 40 kJ mol^{–1} for 3c–5e boryl radicals to 80 kJ mol^{–1} for 4c–7e ones (Figure 3).

Lewis bases

The σ -donating and π -accepting Lewis bases, like pyridine and NHC, interact with boryl radicals in a similar fashion and do not have any substantial difference in stabilization effects.

Therefore, their derivatives and other Lewis bases with analogous conjugated constructs should be considered for designing new stable boryl radicals.

Substituents

Electron-donating substituents can lower the bond strength of the forming B–H bond more efficiently. Consequently, nitrogen-containing substituents are shown to be good candidates for designing more stable boryl radicals.

Reaction characteristics

The reactivity of a boryl radical is boryl based in nature, irrespective of how low the spin density on boron is, because the boron is the only atom that is not in a stable configuration. Although boryl radicals are considered to be highly reactive species and their properties are difficult to control, this work, in combination with recent developments in this area, has clearly shown that it is possible to effectively modulate the structure and reactivity of boryl radicals by incorporating suitable stabilizing substituents and Lewis bases. Much like other more common radicals based on carbon, oxygen, or nitrogen, boryl radicals might serve as intermediates in versatile reactions or even as stable chemicals under ambient conditions, as long as properly designed stabilization measures are taken. The unique reactivity of these new species may finally enrich the toolbox for organic synthesis and polymer chemistry.

Computational Details

Density functional calculations by using the Gaussian 09 package^[7] at the (U)MPW1K^[8]/6-31+G(d)^[9] level were carried out for all of the molecular species under the ideal gas assumption. A geometry optimization and frequency calculation by using the harmonic oscillator model were employed to identify stable molecular structures and the corresponding energy minima. Electronic energies, corrected with the zero-point vibrational energies, were used to calculate the binding energy. The chosen computational method has been proven to be accurate in getting geometric parameters for zwitterionic systems.^[4b,10] The absolute binding energy was not our primary concern, whereas the trend in the binding energies was the main object to explore. Natural bond orbital analyses of charge and spin density on atoms were carried out by using the NBO software.^[11]

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