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Quaternizing Diboranes(4): Highly Divergent Outcomes and an Inorganic Wagner–Meerwein Rearrangement

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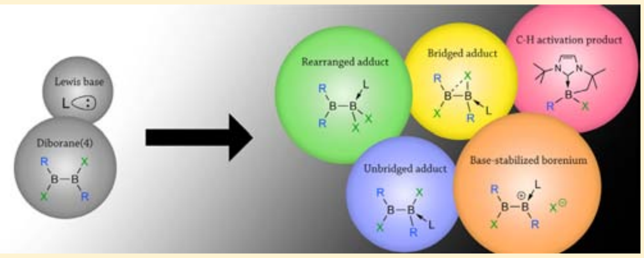
Supporting Information



ABSTRACT: Apart from a few compounds under heavy use in organic chemistry, diboranes are relatively exotic and poorly understood. Recently, interest in these molecules has intensified with the advent of so-called "sp^2-sp^3" diboranes which exhibit useful reactivity toward organic substrates. In our hands, addition of Lewis bases to dihalodiorganyl diboranes(4) has previously shown some very surprising reactivity, including a substituent exchange between the boron atoms, and diboranes in which halide atoms bridge the B–B bond. Herein we have expanded the range of diborane(4) and Lewis base reaction partners, in the process uncovering three new reactivity patterns as well as some cases where mixtures are obtained. Trends are established for the preferential formation of certain products which rationalize the results based on electronic and steric effects. The substituent exchange, clearly based on an inorganic version of the well-known Wagner–Meerwein rearrangement, was also found to be an equilibrium reaction with the halide-bridged Lewis adducts on the other side.

■ INTRODUCTION

The vastly disparate levels of interest in chains of carbon (i.e., organic chemistry) and hypovalent boron belies their proximity on the periodic table. Synthetic and structural understanding of organic compounds has reached a stunning level of sophistication,[1] while in contrast, even compounds as simple as diboranes(4) are still poorly understood. Diboranes(4), despite their increasing popularity in organic chemistry,[2] still suffer from synthetic limitations and unexplored reactivity. The many recent surprises in diborane(4) chemistry, particularly with regard to their interaction with Lewis bases, serve as regular reminders of how little we know these compounds. In the 1990s, the groups of Marder and Norman[3] explored the chemistry of single and double pyridine adducts of diboranes(4). More recently, the groups of Santos,[4] Hoveyda,[5] Gulyás, Bo and Fernández,[6] Hodgkinson, and Lin and Marder[7] have noted changes in reactivity of diboranes when one of the boron atoms is tetracoordinate, particularly in conjugate addition and diboration reactions. Currently, these research groups are changing the way we think about diboranes, and the field now known as sp^2-sp^3 diboranes is very promising indeed.

In 2011, we reported the 1,2-exchange of a mesityl group with a chloride upon addition of an N-heterocyclic carbene (NHC) to a diborane(4).[8] Recently we also discovered a diborane in which one bromide substituent bridged the two boron atoms upon addition of a phosphine, followed by a halide-bridged diborane resulting from a C–H activation of triethylamine.[9] It seems obvious that such a halide-bridged compound is an intermediate in the mesityl/halide 1,2-exchange.

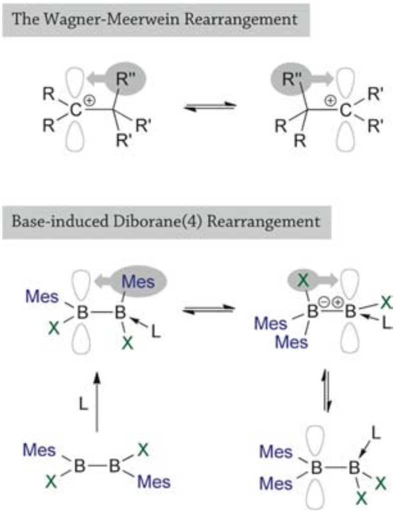


Figure 1. Comparison of the Wagner–Meerwein rearrangement with the proposed mechanism of the recently reported base-induced diborane(4) rearrangement. L = Lewis base.

The 1,2-halide/mesityl exchange reaction of diboranes(4) in the presence of a Lewis base is reminiscent of the 1,2-sigmatropic shift that occurs during the generation of a carbocation in strained alkane systems, known as the Wagner–Meerwein rearrangement.[10] In both cases a substituent migrates from an sp^3 atom to an adjacent atom bearing an empty p orbital (Figure 1), although

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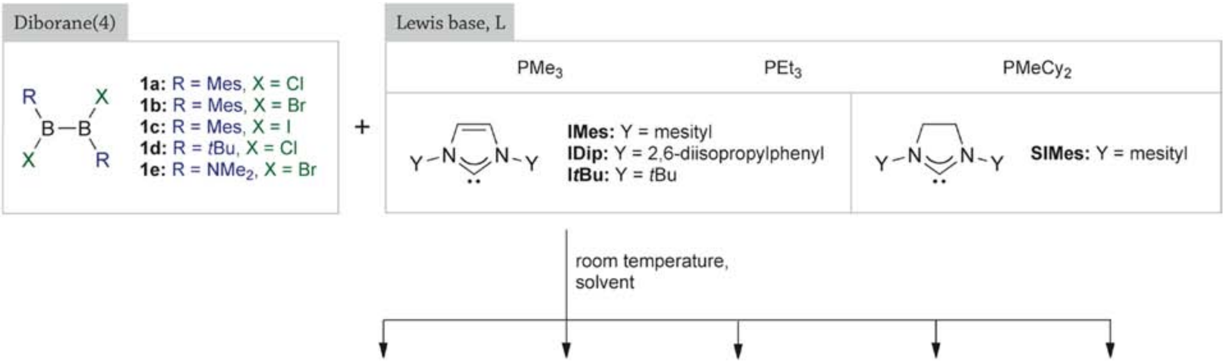


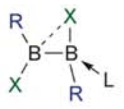
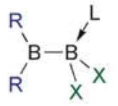
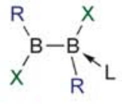
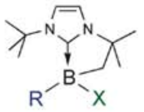
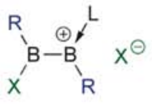
	a: Bridged adduct	**b:** Rearranged adduct	**c:** Unbridged adduct	**d:** C-H activation product	**e:** Base-stabilized borenium
					
2: R = Mes; X = Cl; L = PMe_3 **3:** R = Mes; X = Br; L = PMe_3 **4:** R = Mes; X = I; L = PMe_3	**2a** **3a** **4a**	not detected	not detected	not detected	not detected
5: R = Mes; X = Cl; L = PEt_3 **6:** R = Mes; X = Br; L = PEt_3 **7:** R = Mes; X = I; L = PEt_3	**5a** (93%) **6a** (90%) **7a** (87%)	**5b** (7%) **6b** (10%) **7b** (13%)	not detected	not detected	not detected
8: R = Mes; X = Cl; L = $PMeCy_2$ **9:** R = Mes; X = Br; L = $PMeCy_2$ **10:** R = Mes; X = I; L = $PMeCy_2$	**8a** (34%) **9a** (15%) **10a** (6%)	**8b** (66%) **9b** (85%) **10b** (94%)	not detected	not detected	not detected
11: R = Mes; X = Cl; L = SIMes **12:** R = Mes; X = Br; L = SIMes **13:** R = Mes; X = Cl; L = IDip	not detected	**11b** **12b** **13b**	not detected	not detected	not detected
14: R = tBu; X = Cl; L = PMe_3 **15:** R = tBu; X = Cl; L = PEt_3 **16:** R = tBu; X = Cl; L = IMes **17:** R = tBu; X = Cl; L = SIMes	not detected	not detected	**14c** **15c** **16c** **17c**	not detected	not detected
18: R = tBu; X = Cl; L = ItBu	not detected	not detected	not detected	**18d**	not detected
19: R = NMe_2; X = Br; L = SIMes **20:** R = NMe_2; X = Br; L = IDip	not detected	not detected	not detected	not detected	**19e** **20e**

Figure 2. Reaction of 1,2-dihalodiboranes(4) with Lewis bases leads to a range of different classes of compounds. Compound numbers in red denote those that have been published previously. Percentages in parentheses are the relative amounts of each isomer measured by NMR.

in the diborane case this rearrangement must occur twice to provide the products.

This article contains an exploration of the reactivity of dihalodiboranes(4) in the presence of a range of phosphine and NHC Lewis bases. This reaction results in an astounding diversity of products, which can be favored or disfavored by altering the diborane(4) substituents or the Lewis base. We investigate the scope and mechanism of the 1,2-exchange reaction with reference to the Wagner–Meerwein rearrangement and determine the preferences of each diborane substrate for the halide-bridged or rearranged adducts. We also provide experimental confirmation that in some cases an equilibrium exists between these two isomers. Depending on the reagents, adducts both with and without bridging halide groups can be observed, while other combinations lead to halide displacement and borenium formation, or C–H activation of a carbene side-group.

■ RESULTS AND DISCUSSION

Synthetic Studies. In contrast to our previously reported additions of Lewis bases to diboranes(4),[8,9] addition of the small Lewis base PMe_3 to mesityl diboranes(4) **1a–c** led exclusively to the halide-bridged adducts **2a**, **3a**, and **4a** (Figure 2). No rearranged adducts were detected either by NMR spectroscopy or X-ray crystallography. When the slightly larger base PEt_3 was added to the diboranes **1a–c**, inseparable mixtures of halide-bridged and rearranged adducts **5a/b**, **6a/b** and **7a/b** were formed, respectively. In each case, the halide-bridged adduct (**5a**/**6a**/**7a**) predominated in C_6D_6 solution (87–93% relative to total yield as judged by ^1H NMR spectroscopy). The relative preference for rearrangement increases as the halide becomes heavier (Cl < Br < I). When the more sterically hindered phosphine $PMeCy_2$ was applied to the diboranes(4) **1a–c**, mixtures are again obtained, however the isomeric preference is flipped. In these reactions the rearranged adducts (**8b**/**9b**/**10b**) are preferred over the halide-bridged adducts (**8a**/**9a**/**10a**). As in the compounds **5–7**, the relative preference for rearrangement increases as the halide becomes heavier. Interestingly, for the compounds which were observed as mixtures (**5–10**), the product ratios did not change at lower temperatures as judged by variable-temperature NMR experiments. When much larger NHCs IDip and SIMes are added to the diboranes(4) **1a** and **1b**, the rearranged adducts **11b**/**12b**/**13b** are the exclusive products. Overall, these results show a very clear trend for an increasing preference for rearrangement with increasing size of the Lewis base, from no rearrangement with PMe_3 to complete rearrangement with large NHCs. A large base appears to be a requirement for the rearrangement, perhaps as a way of "pushing" one halide closer to the second boron atom. It should be noted here that the solid material obtained from the reactions of **1a**−**c** with phosphines PEt_3 or $PMeCy_2$ showed slightly different isomeric ratios when dissolved in CD_2Cl_2. This suggests that the relative amounts of each isomer in the mixtures are not static and that the two isomers may exist in an equilibrium, the position of which is slightly different in a different solvent.

The *tert*-butyl-substituted diborane(4) **1d** provides a distinct contrast to the above reactivity. Treating **1d** with PMe_3, PEt_3, IMes or SIMes leads to the simple, unbridged adducts **14c**/**15c**/**16c**/**17c**, regardless of the size or nature of the Lewis base. As a rationale for this behavior, we cannot ignore the fact that the organyl substituents (mesityl) which migrate have sp^2 carbon atoms bound to the boron centers, while those that do not migrate (*tert*-butyl) have sp^3 carbon atoms. The latter are presumably much less likely to form three-membered CBB transition states (dictating a pseudopentacoordinate carbon atom) that were calculated to be intermediates in this migration.[9] The lack of halide bridging is presumably due to the chloride substituent's lower propensity toward bridging combined with the lower steric bulk of the *tert*-butyl group (i.e., a lack of methyl groups that point toward the boron atoms as in the mesityl-substituted compounds).

Table 1. Summary of Spectroscopic Data for the Products of the Base-Addition Reactions[a]

	solvent	^{11}B (BRX/BR_2)	^{11}B ($L\rightarrow B$)	^{31}P
		Halide-Bridged Adducts, **a** Series		
2a	C_6D_6	80.8	−4.11	−9.37
3a	CD_2Cl_2	56.5	−2.31	−10.4
4a	C_6D_6	41.8	1.61	−14.3
5a	C_6D_6	81.0	−2.50	3.64
	CD_2Cl_2	75.4	−2.77	3.54
6a[7]	C_6D_6	58.1	−1.62	0.19
7a	C_6D_6	37.1	2.30	−2.24
	CD_2Cl_2	37.1	4.70	−0.14
8a	C_6D_6	80.8	−1.02	−2.26
9a[7]	C_6D_6	60.3	−0.43	−1.45
	CD_2Cl_2	61.0	1.30	−1.97
10a	C_6D_6	n.d.	n.d.	−4.28
		Rearranged Adducts, **b** Series		
5b	C_6D_6	n.d.	n.d.	2.11
	CD_2Cl_2	94.6	n.d.	2.16
6b[7]	C_6D_6	91.0	−7.87	−0.25
7b	C_6D_6	90.0	n.d.	−3.36
	CD_2Cl_2	90.3	−20.4	−3.04
8b	C_6D_6	93.6	−1.02	−2.26
9b[7]	C_6D_6	95.5	−6.74	−4.76
	CD_2Cl_2	94.6	−6.62	−4.35
10b	C_6D_6	88.6	−20.8	−8.93
11b[6]	CD_2Cl_2	87.4	−0.17	n.a.
12b	CD_2Cl_2	79.7	−5.03	n.a.
13b	CD_2Cl_2	85.3	0.60	n.a.
		Unbridged Adducts, **c** Series		
14c	C_6D_6	95.2	−1.89	−13.18
15c	C_6D_6	95.0	−1.2	3.3
16c	C_6D_6	93.9	−1.5	n.a.
17c	C_6D_6	91.4	−1.3	n.a.
		C−H Activation Product, **d** Series		
18d	C_6D_6	n.a.	3.42	n.a.

[a] n.d. is not determined; n.a. is not applicable; and chemical shifts are expressed in ppm.

Although the addition of Lewis bases to the diborane(4) **1d** led in four cases to simple, unbridged adducts, attempting this reaction with the NHC I*t*Bu (1,3-bis-(*tert*-butyl)imidazol-2-ylidene) provided an unexpected product. The white solid obtained had one high-field ^{11}B NMR signal, and the ^1H NMR spectrum indicated that only one B-*t*Bu group was present per NHC unit. Single crystal X-ray crystallography (see Supporting Information) indicated that a C−H bond of one carbene *tert*-butyl group, as well as the B−B bond, had been cleaved, resulting in the bicyclic species **18d** (Figure 2). Based on this formula, a yield of 97% was calculated. We had earlier reported the synthesis of a similar bicyclic species,[8] however, this was prepared using monoborane starting materials. Although it was not detected, the presumed byproduct of this reaction is the monoborane HBCl(*t*Bu) or a dimer thereof.

The boron atoms of 1,2-diamino-1,2-dihalodiboranes(4) were expected to be reluctant to accept Lewis base donation, given the effective π donation from the amino groups. Thus the reaction of **1e** with the carbene IDip led to divergent products from the displacement of the bromide by the carbene. These products, **19e** and **20e** (Figure 2), are the first known base-stabilized borenium cations based on a diborane backbone (i.e., diborenium cations).[11]

Spectroscopic Studies. Selected ^{11}B and ^{31}P NMR spectroscopic data for the compounds/mixtures **2**−**18** can be found in Table 1. The most apparent features of these data are the high-field ^{11}B signals (δ −20.8 to 4.70) for the base-stabilized, quaternary boron atoms and the low-field signals (δ 37.1 to 95.5)

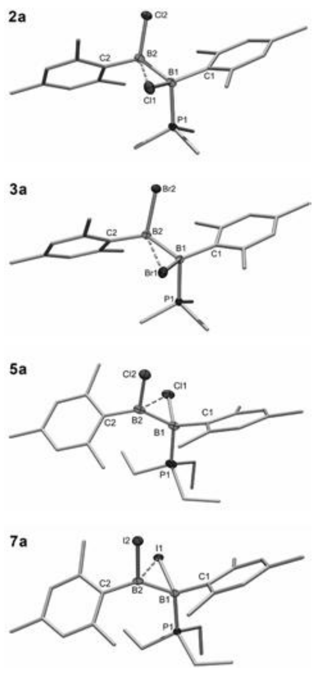


Figure 3. Molecular structures of **2a**, **3a**, **5a**, and **7a**. Thermal ellipsoids represent 50% probability. Aryl and alkyl substituents have been simplified for clarity. Selected bond lengths and angles can be found in Table 2.

for the nonbase-stabilized boron atoms. In most cases, these signals are very broad as a result of $^{11}B-^{11}B$ coupling. The distance between the two signals for each compound is also much larger for the compounds without halide bridging (**b** and **c** series) than those of the halide-bridged isomers (**a** series). Presumably the bridging halide atoms exert a "quaternizing" effect on the secondary boron atoms, resulting in higher-field ^{11}B NMR signals. The tricoordinate boron nuclei of the unbridged adducts **14c**/**15c**/**16c**/**17c** show ^{11}B NMR signals (δ 91−95) further downfield of those of the precursor diborane(4) (δ 84.3),[12] a strong indication that no bridging halide is present in solution. The ^{31}P NMR signals of the phosphine adducts for the most part lie in a small range on either side of zero (δ −14.3 to 3.64). No significant distinction in the ^{31}P NMR properties can be observed between the **a**, **b**, or **c** series. The C−H activated product **18d** exhibits an ^{11}B NMR resonance in the expected range for a quaternary boron nucleus (δ 3.42). Only single ^{11}B NMR signals were found for the base-stabilized diborenium salts **19e** (δ 37.9) and **20e** (δ 37.7). Averaging of the two boron signals due to rapid swapping of the base between boron atoms was ruled out by ^1H and variable-temperature ^{11}B NMR, thus we attribute the single ^{11}B NMR signals to either accidental superimposition of the signals or extreme broadness of the borenium nuclei signal due to B−B coupling, making them invisible.

Structural Studies. Molecular structures of the halide-bridged isomers **2a**, **3a**, **5a**, and **7a** are shown in Figure 3, and the rearranged adducts **8b**, **10b**, **12b**, and **13b** in Figure 4. Selected structural parameters for these compounds can be found in Table 2. The mesityl groups of the halide-bridged isomers are found, in each case, on opposite sides of the B_2 unit. Therefore, while different diastereomers of these molecules are possible in theory, only one is observed, it being a racemic mixture of the two corresponding enantiomers. The two series of compounds (**a** and **b**) have obvious structural differences related to the presence of bridging halide groups. For instance, short B2−X1 distances (2.44−2.62 Å) and acute B2−B1−X1 angles (82.6−87.9°) are found in the **a** series, while the B2−B1−X1 angles are all obtuse in the **b** series. An unexpected difference between the two series is the significantly shorter B1−B2 distances in the **a** series, perhaps also a result of the bridging halide groups.

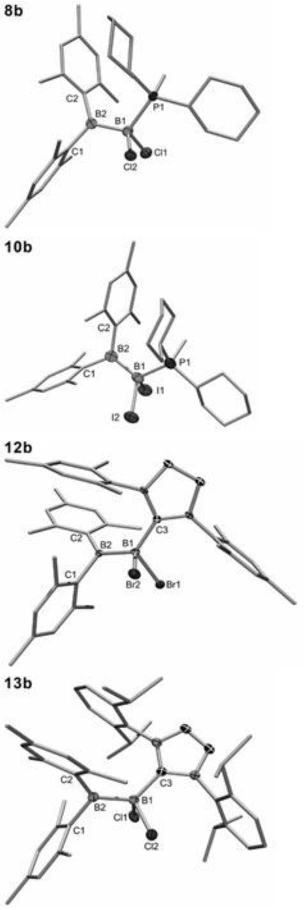


Figure 4. Molecular structures of rearranged adducts **8b**, **10b**, **12b**, and **13b**. Thermal ellipsoids represent 50% probability. Aryl and alkyl substituents have been simplified for clarity. Selected bond lengths and angles can be found in Table 2.

One possible quantifier of the extent of halide bridging in the complexes of the **a** series is the B2−B1−X1 angle. This angle is smaller when the base is larger (i.e., PEt_3 vs PMe_3), and when the base is kept constant, is smaller when the halide is heavier. A second method for measuring this effect is to compare the distance of the weak B2−X1 bond with that of the conventional B2−X2 bond. The parameter Δ_{BX} denotes the d(B2−X1)/d(B2−X2) ratio. As in the B2−B1−X1 angles, this parameter is lower (i.e., stronger bridging) with larger phosphines and heavier halides. However, these Δ_{BX} values are significantly higher than a previously reported diborane, which contained an almost symmetrically bridging iodide group and had a Δ_{BX} value of 1.06.[9b] Both of these metrics point to a higher propensity toward bridging with larger Lewis bases and heavier, more polarizable halides. As expected, the B1−$C_{carbene}$ distances of the NHC adducts **11b**/**12b**/**13b** are much shorter than the B1−P1 distances of comparable phosphine adducts **9b**/**10b**/**11b**, however, the nature of the Lewis base appears to have little effect on the B1−B2 distance in these complexes.

A crystal structure determination of diborane(4) base adduct **15c** showed clearly the absence of a bridging chloride atom, with a B2−B1−X1 angle corresponding to a tetrahedral base-stabilized boron atom. C−H activated species **18d** was found to be structurally

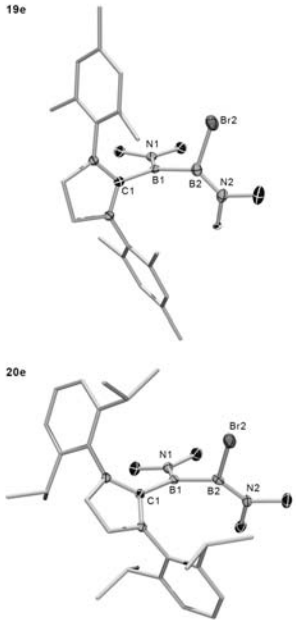


Figure 5. Molecular structures of the base-stabilized borenium salts **19e** (with SIMes) and **20e** (with IDip). Thermal ellipsoids represent 50% probability. Carbene substituents have been simplified and counterions omitted for clarity. Selected bond lengths and angles can be found in Table 2.

Table 2. Summary of Crystallographic Data for the Products of the Base-Addition Reactions[a]

	B1–B2 (Å)	B1–P1/$C_{carbene}$ (Å)	B1–X1 (Å)	B2–X1 (Å)	B2–X2 (Å)	$Δ_{BX}$	B2–B1–X1 (°)
			Halide-Bridged Adducts, **a** Series				
2a	1.721(3)	1.970(2)	1.955(2)	2.555(2)	1.812(2)	1.41	87.85(12)
3a	1.719(3)	1.9753(18)	2.1572(18)	2.6197(19)	1.9820(19)	1.32	84.22(10)
5a	1.715(3)	1.9896(18)	1.9754(18)	2.4439(18)	1.8177(18)	1.34	82.62(9)
6a[7]	1.711(3)	1.990(2)	2.178(2)	2.437(2)	2.004(2)	1.22	76.5(1)
7a	1.711(2)	1.9904(18)	2.3989(17)	2.5867(17)	2.2496(17)	1.15	75.96(8)
			Rearranged Adducts, **b** Series				
8b	1.755(5)	1.975(4)	1.901(4)	n.a.	1.886(4)	n.a.	107.7(2)
9b[7]	1.749(3)	1.988(2)	2.067(3)	n.a.	2.053(2)	n.a.	103.8(1)
10b	1.769(7)	1.967(4)	2.293(4)	n.a.	2.283(4)	n.a.	102.6(2)
11b[6]	1.774(3)	1.653(2)	1.906(2)	n.a.	1.889(2)	n.a.	101.2(1)
12b	1.762(4)	1.652(4)	2.061(3)	n.a.	2.083(3)	n.a.	98.64(15)
13b	1.758(2)	1.639(2)	1.9020(16)	n.a.	1.8994(17)	n.a.	112.24(10)
			Unbridged Adducts, **c** Series				
15c	1.724(4)	2.018(3)	1.945(3)	n.a.	1.816(3)	n.a.	109.9(2)
			C–H Activation Product, **d** Series				
18d	n.a.	1.657(3)	1.9728(19)	n.a.	n.a.	n.a.	n.a.
			Base-Stabilized Borenium Salt, **e** Series				
19e	1.710(3)	1.612(3)	n.a.	n.a.	1.996(3)	n.a.	n.a.
20e	1.707(3)	1.608(3)	n.a.	n.a.	1.984(2)	n.a.	n.a.

[a] For atom numbering see the individual molecular structures in Figures 3 and 4. X = Cl, Br, or I. $Δ_{BX}$ is the ratio of the B2-X1 and B2-X2 distances. This is a way of gauging the extent of the halide bridging relative to an internal B-X standard (i.e. the conventional B2–X2 distance).

similar to the previously reported C–H activation product from a different route.[8] Details of the structure determination of **18d** can be found in the Supporting Information.

The molecular structures of base-stabilized borenium salts **19e** and **20e** are shown in Figure 5, and some parameters are listed in Table 2. The structures show significantly shorter $B-C_{carbene}$ distances (1.612(3) and 1.608(3) Å) than the other carbene-coordinated compounds in this study (**11b**: 1.653(2) Å; **12b**: 1.652(4) Å; **13b**: 1.639(2) Å), understandable given the tricoordinate nature of the boron atoms in the former.

Mechanistic Computational Study. In order to rule out the spontaneous rearrangement of the diboranes(4) in the absence of base, we investigated this possibility by DFT calculations on a computational model of 1,2-dibromo-1,2-dimesityldiborane(4), $\mathbf{1b}_{OPT}$ (Figure 6). These calculations showed that the rearrangement of $\mathbf{1b}_{OPT}$ to the unsymmetrical 1,1-dibromo-2,2-dimesityldiborane(4) ($\mathbf{1b'}_{OPT}$) in the absence of a Lewis base is endothermic by $ΔG = 15.09$ kJ·mol^{-1}. The reaction, through transition state $\mathbf{1b}_{TS}$, involves an activation barrier of $ΔG = 115.22$ kJ·mol^{-1}. This barrier is higher than those found for the Lewis-base-induced rearrangements **6a**→**6b**($ΔG = 96.30$ kJ·mol^{-1})[9] and **9a**→**9b** ($ΔG = 79.37$ kJ·mol^{-1})[9], suggesting that the quaternization of one boron (and hence the Lewis base) is integral to the rearrangement process. Figures illustrating the relative energies of all of these processes can be found in the Supporting Information.

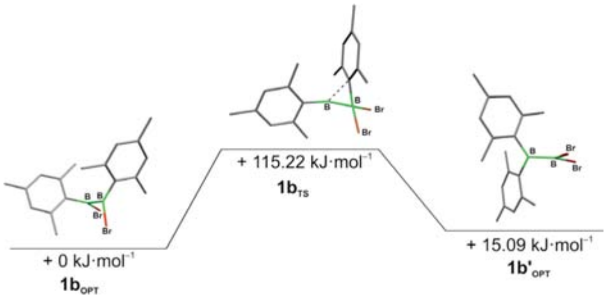


Figure 6. Calculated mechanism for a hypothetical base-free diborane(4) rearrangement process, calculated using the PBE level of theory ($ΔG^{298}$ ($\mathbf{1b'}_{OPT}$) and $ΔG^{‡298}$ ($\mathbf{1b}_{TS}$) energies are shown).

■ CONCLUSION

Our work combining Lewis bases with diboranes(4) has uncovered a truly fascinating unpredictability, as demonstrated by the five distinct classes of compounds (classes **a**–**e**, Figure 2) obtained herein. We have presented spectroscopic and structural data of all five classes and drawn some clear conclusions about the reactivity which should help predict the outcome of future diborane/Lewis base reactions. We also hope our results will be of assistance in the design of sp^2–sp^3 diboranes for use as reagents in organic chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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