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Lithioboranes. A Theoretical Study

Matthias Wagner,[†,§] Nicolaas J. R. van Eikema Hommes,[‡] Heinrich Nöth,[†] and Paul von Ragué Schleyer[‡,*]

Institut für Anorganische Chemie der Ludwig-Maximilians Universität München, Meiserstrasse 1, D-80333 München, FRG, and Computational Chemistry Center, Friedrich-Alexander Universität Erlangen-Nürnberg, Nägelsbachstrasse 25, D-91052 Erlangen, Germany

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High-level *ab initio* calculations (MP4sdtq/6-311+G**//MP2/6-31G*) predict classical structures for monomeric lithioborane and the dimethyl, diamino, and difluoro derivatives. A structure with the lithium cation bridging one boron oxygen bond is computed as the most stable structure for dihydroxylithioborane. For this compound, an "inverted" structure is indicated to be viable. The singlet state of the boryl anion is only marginally more stable than the triplet at levels up to CCSD(T)/6-311+G(3df,2pd), but interaction with a lithium cation stabilizes the singlet more than the triplet by about 20 kcal/mol. Reaction of lithioboranes with formaldehyde, as a model for carbonyl compounds, is predicted to proceed via nucleophilic attack of the boryl anion moiety, through a very early transition structure, to give a B−C−O three-membered-ring product.

Introduction

Lithiated boranes, $LiBR_2$, are an intriguing, though yet experimentally unknown, class of compounds. With the formal negative charge located on the electropositive boron atom, as well as a vacant p orbital, extraordinary bonding situations can be expected. Most boron reagents are electrophiles, but the "umpolung" of lithioboranes would allow them to serve as nucleophiles. Hence, these compounds can have considerable synthetic potential for the preparation of boron-containing molecules.

Our interest in lithioboranes was aroused by recent results in the field of stannylated boranes, which are capable of reacting as nucleophiles, shown as follows:[1]

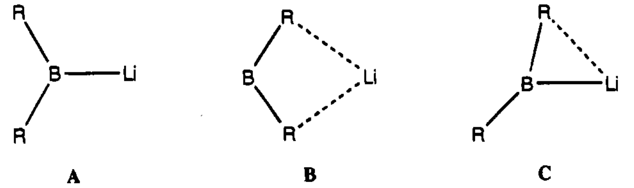
$$(Me_2N)_2B{-}SnMe_3 + C_2H_5I \rightarrow (Me_2N)_2B{-}C_2H_5 + I{-}SnMe_3$$

We have now explored the chemistry of the lithioboranes R_2BLi, R = H, CH_3, NH_2, OH, and F, computationally. The following topics are addressed:

1. The H_2B^- anion is isoelectronic with H_2C:, which has a triplet ground state.[2] What is the ground state of H_2B^-? The singlet state of a carbene is stabilized by π-donating substituents like halogens or amines.[3] Do lithioboranes behave similarly, or does the negative charge on boron inhibit stabilization?

2. What is the character of the boron-lithium bond? Are lithioboranes well represented as ionic species $Li^+BR_2^-$, similar to organolithiums or lithium salts,[4] or does the small difference in electronegativity between boron and lithium lead to a more covalent bonding? We also analyze the interaction between π-donating substituents and boron by the natural bond orbital method.[5]

3. Substitution on boron will influence the stability of the boranes and, to different extents, of the lithioboranes. What effect does this have on their Brønsted acidities? Furthermore, structural alternatives to the classical structural type **A**, which is found for the parent H_2BLi system,[6] also can be expected when electronegative substituents are present. Inverted structures **B**, in which the lithium cation interacts only with the substituents, or structures **C**, in which lithium occupies a bridging position with interactions both to boron and to a more electronegative atom, may well be competitive energetically.



4. Do lithioboranes react as nucleophiles or as electrophiles? The mechanisms of reaction of the parent compound, H_2BLi, and the dimethyl and difluoro derivatives, $(CH_3)_2BLi$ and F_2BLi, with formaldehyde (as a model for carbonyl compounds), are computed.

Computational Details

Ab initio calculations were performed using the Gaussian 90[7a] and Gaussian 92[7b] program packages. All geometries were optimized both at HF/6-31G* and MP2(fu)/6-31G* level and characterized as minima, saddle points, etc. by calculation of vibrational frequencies at HF/6-31G*. In the study of the reaction with formaldehyde, the structures were refined at the MP2(fc)/6-31+G* level. Relative energies for the various isomers and for the reaction of H_2BLi with formaldehyde were computed at MP4SDTQ/6-311+G** using the MP2 optimized geom-

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[†] Universität München.

[‡] Universität Erlangen-Nürnberg.

[§] Present address: Technische Universität München, Anorganisch-chemisches Institut, Lichtenbergstr. 4, D-85747 Garching bei München, Germany.

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(1) Horchler, K.; Nöth, H.; Storch, W.; Wagner, M. Unpublished results. See also: Wagner, M. Ph.D. Thesis ("Doktorarbeit"), Universität München, 1992.

(2) Schaefer, H. F., III. *Science* **1986**, *231*, 1100.

(3) Regitz, M. *Angew. Chem.* **1991**, *103*, 692; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674. See also, e.g.: Wentrup, C. *Reactive Molecules*; J. Wiley & Sons: New York, 1984; p 162 ff. Jones, M., Jr.; Moss, R. A. *Reactive Intermediates*; J. Wiley & Sons: New York, 1981; Vol. 2, p 60 ff.

(4) See: Sapse, A. M.; Schleyer, P. v. R. *Lithium Compounds*: *Principles and Applications*; J. Wiley & Sons: New York, 1994.

(5) (a) NBO analysis: Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899 and references cited therein. (b) NLMO bond orders: Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434. (c) NPA charges: Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(6) See e.g.: Boggs, J. E.; Cordell, F. R. *J. Mol. Struct. THEOCHEM* **1981**, *76*, 329. Ha, T.-K. *J. Mol. Struct. THEOCHEM* **1986**, *36*, 165.

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Table 1. Selected Geometrical Parameters (MP2(fu)/6-31G*) for $LiBR_2$ and HBR_2 Isomers (R = H, CH_3, F, OH, NH_2; X = H, C, F, O, N)[a]

struct	B−Li	X^1−Li	B−X^1	B−X^2	∠LiBX^1	∠XBX
1			1.191			120.0
2a	2.225		1.207		124.6	110.8
2b	1.876	2.039	1.179		80.2	160.4
2a−t	2.118		1.191		111.3	137.5
2c−t	2.004	1.860	1.216	1.184	65.3	129.5
3			1.567			123.4
4a	2.270		1.582			114.2
4b	4.005		1.541			122.4
5			1.325			118.4
6a	2.221		1.353			111.6
6b	2.374	1.777	1.483		48.1	96.7
6c	2.047	1.835	1.472	1.323	60.3	100.8
7			1.363	1.373		119.3
7′			1.366			116.5
7″			1.371			125.8
8a	2.220		1.388	1.392	109.5	112.9
8a′	2.223		1.385			111.3
8a″	2.209		1.392			118.8
8b	2.369		1.468			99.4
8c	2.058	1.835	1.447	1.375	60.2	110.7
8c″	2.072	1.855	1.457	1.367	60.5	117.1
8ts	2.151	2.597	1.401	1.385	91.4	113.2
9			1.416			122.7
9′			1.393	1.485		117.5
9″			1.485			123.7
10a	2.247		1.429			116.1
10a′	2.251		1.505			119.6
10b	2.424		1.563		52.8	105.6
10b′	2.126		1.416		64.5	129.0
10c	2.062		1.568	1.398	63.2	115.0

[a] Distances in Å; angles in degrees.

etries. Unless indicated otherwise, relative energies given in the text are at the highest available level of theory and are corrected for differences in zero point energy, calculated at HF/6-31G* and scaled by 0.91.[8] Atomic charges, bond orders, and orbital interaction energies were calculated using the natural population analysis (NPA) and natural bond orbital analysis (NBO) methods.[5]

Results and Discussion

Figure 1 shows the structures of the lithioboranes discussed in this study. Selected geometrical parameters, total and zero point vibrational energies, relative energies, and selected electronic properties are given in Tables 1−4.

The Boryl Anion. Electronic States. Methylene, isoelectronic with the free boryl anion, has a triplet ground state. The experimental singlet−triplet separation of 9.05 ± 0.06 kcal/mol [9] can only be reproduced calculationally at very high levels of theory.[2] The singlet−triplet separation generally is overestimated. A high degree of sophistication also is necessary to characterize the ground state of the boryl anion. Indeed, the singlet and triplet states have very similar energies, the triplet being 0.20 kcal/mol more stable at CCSD(T)/6-311+G(3df,2pd) + ΔZPE//MP2(fu)/6-31+G**. However, due to the use of a finite basis set and the incomplete treatment of correlation, the stability of the singlet state is underestimated systematically and a correction for the different number of paired electrons is necessary: the difference between the "exact" dissociation energy of H_2, 0.17447 au,[10] and the value calculated at the level used in the present study is added to the absolute energy of the singlet state.[11] At CCSD(T)/6-311+G(3df,2pd), this correction is −1.12 kcal/mol. Hence, our final estimate of the energy difference is 0.92 kcal/mol, favoring the singlet.

Bent structures are computed both for the singlet and for the triplet state of the boryl anion. At CISD/6-311+G**, the calculated HBH angle is 103.5° for the singlet, while a much larger angle of 128.5° is computed for the triplet. A similar effect of the electronic state is present in methylene. At the same level, the HCH angle in singlet CH_2 is 101.5°, while 133.0° is computed for triplet CH_2.

Coordination of the boryl anion to a lithium cation stabilizes the singlet state relative to the triplet. At MP4/6-311+G**//MP2(fu)/6-31G* + ΔZPE, singlet lithioborane **2a** is 16.0 kcal/mol lower in energy than the triplet **2c−t**; at QCISD(T), the difference is 16.4 kcal/mol. Again, these values must be corrected for incomplete treatment of correlation, as described above. The corrections are 4.0 and 3.6 kcal/mol, respectively, so that the final estimate of the energy difference is 20.0 kcal/mol. We conclude that lithioboranes will have singlet ground states. Hence, the triplet states have not been considered further in this study.

Lithioborane and Lithiodimethylborane. The parent lithioborane, H_2BLi (**2**), as well as the methyl-substituted derivative $(CH_3)_2BLi$ (**4**), show a distinct preference for a classical structure, type **A**, with a moderately covalent boron−lithium bond. The alternative inverted structures, type **B**, are not competitive energetically. They are not even minima on the RHF/6-31G* potential energy surface. At MP4/6-311+G**//MP2(fu)/6-31G* + ΔZPE, the inverted structures of H_2BLi (**2b**) and $(CH_3)_2BLi$ (**4b**) are 57.5 and 35.9 kcal/mol higher in energy than the corresponding classical structures **2a** and **4a**.

Two significant changes in geometry occur upon lithation at boron. The B−C and B−H bonds in **2a** and **4a** are elongated relative to the corresponding boranes **1** and **3**, by 0.016 and 0.015 Å, respectively, and the angle between the substituents is contracted strongly, by 9.2°. These geometrical changes resemble the tendency toward pyramidalization in carbanion chemistry.[12] In line with Bent's rule,[13] the boron−lithium bond has more s character than the boron−hydrogen bond. The other bonds will have more p character and, consequently, be longer, with smaller bond angles.

The B−Li bond has significant covalent character in these species. In H_2BLi (**2a**), the NLMO/NPA bond order,[5b] which provides a measure for the degree of covalency, is 0.31. The NPA charge[5c] on lithium is +0.68. Similar values are computed for $(CH_3)_2BLi$ (**4a**): the B−Li bond order is 0.36, and the lithium charge is +0.64. However, the distribution of the negative charge differs substantially between these species. In H_2BLi (**2a**), more than half of the negative charge is located on boron (−0.37), while, in $(CH_3)_2BLi$ (**4a**), the boron atom is positively charged (+0.19) and the negative charge is localized on the methyl groups (−0.42 each).

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(7) (a) Gaussian 90, Revision I: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990. (b) Gaussian 92: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

(8) Grev, R. S.; Jansen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1991**, *95*, 5128 and references cited therein.

(9) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251.

(10) Kolos, W.; Wolniewiecz, L. *J. Chem. Phys.* **1968**, *49*, 404.

(11) See: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; J. Wiley & Sons: New York, 1986.

(12) Boese, R.; Bläser, D.; Niederprüm, N.; Nüsse, M.; Brett, W. A.; Schleyer, P. v. R.; Bühl, M.; van Eikema Hommes, N. J. R. *Angew. Chem.* **1992**, *104*, 356; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 314.

(13) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

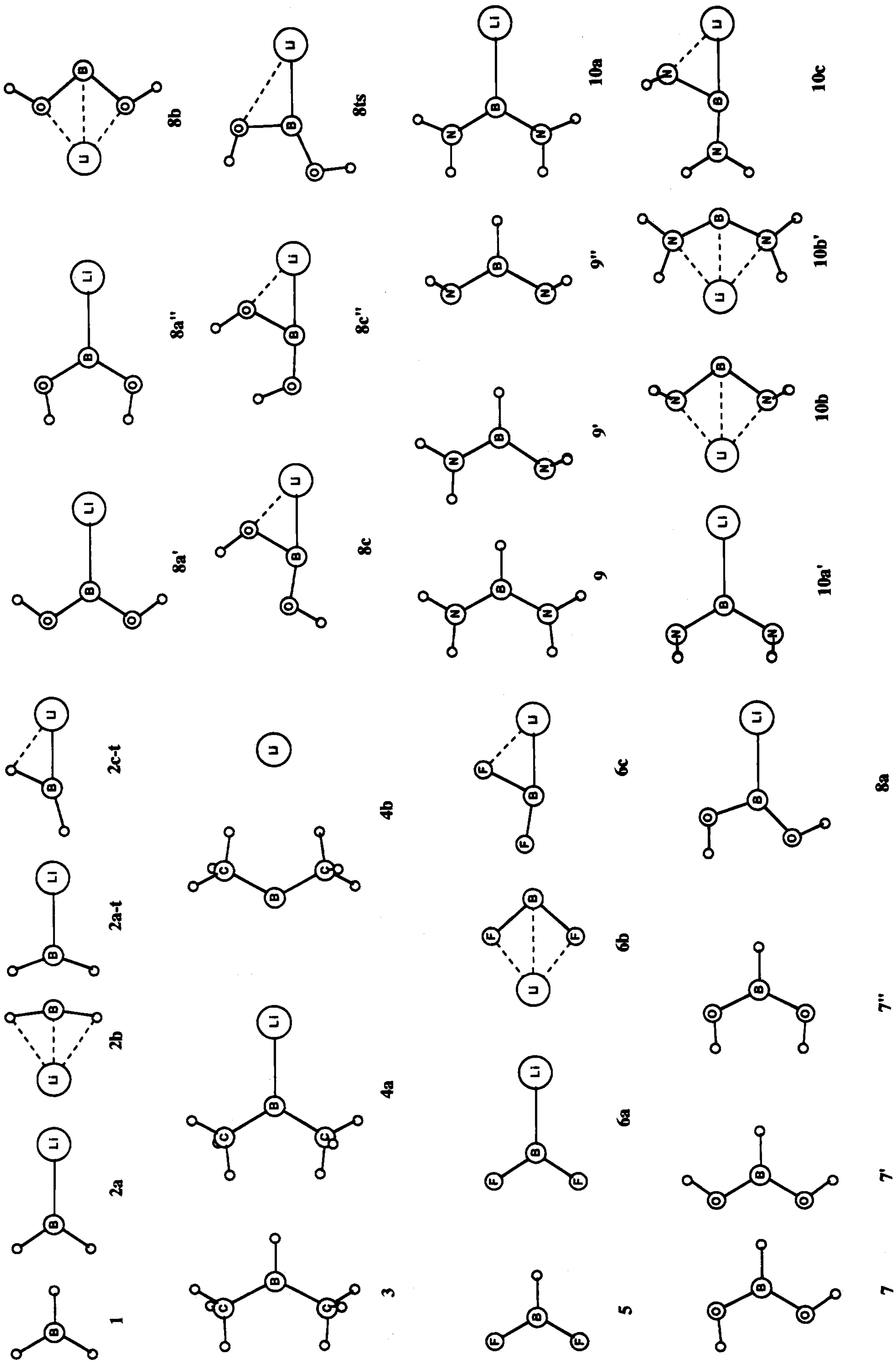
1
2a
2b
2a-t
2c-t
3
4a
4b
5
6a
6b
6c
7
7'
7"
8a
8a'
8a"
8b
8c
8c"
8ts
9
9'
9"
10a
10a'
10b
10b'
10c

Figure 1.

Table 2. Absolute Energies (au) and Zero Point Vibrational Energies (kcal/mol) for $LiBR_2$ and HBR_2 Isomers (R = H, CH_3, F, OH, NH_2)

struct	point group	HF/6-31G*	ZPE//6-31G*	MP2(fu)/6-31G*	MP2(fc)/6-31+G*	MP4(fc)/6-311+G**
1	D_{3h}	−26.390 01	17.38(0)	−26.468 57	−26.465 48	−26.518 26
2a	C_{2v}	−33.209 94	11.72(0)	−33.297 09	−33.294 65	−33.346 17[a]
2b	C_{2v}	−33.102 37	11.07(1)	−33.197 89		−33.253 71
2a−t	C_{2v}	−33.191 85	10.58(1)	−33.266 80		−33.313 60
2c−t	C_s	−33.167 34	11.36(0)	−33.273 30		−33.320 12[a]
3	C_2	−104.492 63	56.49(0)	−104.843 09		−104.980 70
4a	C_2	−111.302 25	50.75(0)	−111.665 90	−111.657 68	−111.801 55
4b	C_2	−111.222 07	48.99(3)	−111.601 60		−111.741 86
5	C_{2v}	−224.262 40	12.05(0)	−224.688 62		−224.849 81
6a	C_{2v}	−231.089 36	5.79(0)	−231.526 10	−231.541 65	−231.688 77
6b	C_{2v}	−231.068 58	4.96(0)	−231.511 70	−231.520 28	−231.668 79
6c	C_s	−231.085 08	5.49(0)	−231.526 77	−231.535 52	−231.683 66
7	C_s	−176.253 37	28.61(0)	−176.697 72	−176.704 00	−176.849 71
7′	C_{2v}	−176.250 11	28.53(0)	−176.694 60	−176.700 90	−176.847 52
7″	C_{2v}	−176.247 33	28.32(0)	−176.691 70	−176.697 69	−176.843 74
8a	C_s	−183.068 76	22.44(0)	−183.526 82		−183.675 19
8a′	C_{2v}	−183.062 79	22.58(0)	−183.521 00		−183.672 66
8a″	C_{2v}	−183.062 27	21.88(0)	−183.520 72		−183.671 65
8b	C_{2v}	−183.059 24	22.14(0)	−183.521 40		−183.673 11
8c	C_s	−183.072 48	22.20(0)	−183.533 71		−183.680 38
8c″	C_s	−183.060 70	21.41(0)	−183.522 57		−183.669 99
8ts	C_s	−183.066 39	21.95(1)	−103.526 19		−183.676 10
9	C_{2v}	−136.568 30	44.28(0)	−136.983 90		−137.126 24
9′	C_s	−136.546 27	44.00(1)	−136.962 12		−137.105 39
9″	C_{2v}	−136.498 38	41.98(2)	−136.908 93		−137.055 08
10a	C_{2v}	−143.373 69	37.90(0)	−143.803 67		−143.943 77
10a′	C_{2v}	−143.308 77	35.64(2)	−143.734 48		−143.881 23
10b	C_{2v}	−143.323 01	37.07(2)	−143.758 53		−143.899 71
10b′	C_{2v}	−143.279 06	36.22(2)	−143.734 92		−143.875 13
10c	C_s	−143.362 03	37.93(1)	−143.795 62		−143.925 08

[a] QCISD(T)/6-311+G** values: **2a**, −33.348 30; **2a**−T−, −33.321 68.

Table 3. Relative Energies (kcal/mol) for $LiBR_2$ and HBR_2 Isomers (R = H, CH_3, F, OH, NH_2)

struct	HF/ 6-31G*	MP2(fu)/ 6-31G*	MP2(fc)/ 6-31+G*	MP4(fc)/ 6-311+G**	MP4 incl ΔZPE//6-31G*
2a	0.00	0.00		0.00	0.0
2b	67.50	62.25		58.02	57.5
2a−t	11.35	19.01		20.44	19.4
2c−t	26.73	14.93		16.35	16.0
4a	0.00	0.00		0.00	0.0
4b	50.31	40.35		37.46	35.9
6a	0.00	0.42	0.00	0.00	0.0
6b	13.04	9.46	13.41	12.54	11.8
6c	2.69	0.00	3.85	3.21	2.9
7	0.00	0.00	0.00	0.00	0.0
7′	2.05	1.96	1.95	1.37	1.3
7″	3.79	3.78	3.96	3.75	3.5
8a[a]	2.33	4.32		3.26	3.5
8a′	6.08	7.98		4.84	5.2
8a″	6.41	8.15		5.48	5.2
8b	8.31	7.72		4.56	4.5
8c	0.00	0.00		0.00	0.0
8c″	7.39	6.99		6.52	5.8
8ts	3.82	4.72		2.69	2.5
9	0.00	0.00		0.00	0.0
9′	13.82	13.67		13.08	12.8
9″	43.88	47.04		44.65	42.6
10a	0.00	0.00		0.00	0.0
10a′	40.74	43.42		39.24	37.2
10b	31.80	28.33		27.65	26.9
10b′	59.38	43.14		43.07	41.5
10c	7.32	5.05		11.73	11.8

[a] See text.

Boranes and Lithioboranes with Electronegative Substituents. Replacement of hydrogen or alkyl substituents on boron by electron-withdrawing groups changes the characteristics both of the boranes and of their lithiated derivatives. Interaction of the substituent lone pairs with the formally empty p_z orbital on boron leads to some double bond character and a preference for planar conformations. Lithiation will increase the charge density on boron, which will counteract π donation by the substituents. Further, the substituents may coordinate to the lithium cation. This will increase the stability of bridged structures, type **C**, but may make a lone pair unavailable for π donation into the empty p orbital on boron.

The interactions between lone pairs and the boron p_z orbital can be described as "delocalizations" from the ideal Lewis structure. The natural bond orbital analysis method provides an estimate of the energy associated with these delocalizations by means of second-order perturbational theory. In the present work, these interaction energies are too large to allow a quantitative interpretation, so that only qualitative trends will be discussed.

Difluorolithioborane prefers a classical structure, type **A**, but compared to lithioborane (**2**) and lithiodimethylborane (**4**), the difference between **6a** and the alternative structures **6b** and **6c** is much smaller. At MP2(fu)/6-31G*, **6c** is even more stable than **6a** by 0.4 kcal/mol, but this is caused by basis set superposition error (BSSE). When the basis set is augmented with diffuse functions, or when the larger 6-311+G* basis set is used, the energetic order changes back in favor of **6a**. At MP4/6-311+G*//MP2(fu)/6-31G* + ΔZPE, bridged **6c** is 2.9 kcal/mol higher in energy than **6a**, while the inverted structure **6b** is 11.8 kcal/mol less stable. All structures are minima at HF/6-31G*.

The structural changes upon going from difluoroborane (**5**) to difluorolithioborane (**6a**) are similar to those seen for **2a** and **4a**. The B−F bonds are elongated by 0.028 Å, and the F−B−F angle is reduced by 6.8°. The negative NPA charge on fluorine increases somewhat, from −0.55 in **5** to −0.61 in **6a**. The weakening of the B−F bond upon lithiation is reflected in the NLMO/NPA bond order, which is decreased by 0.06 to 0.38. π-Donation by fluorine also is lower in **6a** than in difluoroborane, and the boron p_z occupancy is reduced by 0.01 e to 0.18 e.

Table 4. Selected Electronic Properties of $LiBR_2$ and HBR_2 Isomers (R = H, CH_3, F, OH, NH_2)

	NBO charges					NLMO bond orders			ΔE^2 deloc[a]	
struct	B	Li	X^1 [b]	X^2 [b]	boron p_z occ[c]	B−Li	B−X^1	B−X^2	$X^1 \rightarrow B$	$X^2 \rightarrow B$
2a	−0.37	0.68	−0.15			0.31	0.83			
2c−t	0.55	0.89	−0.21	−0.13		0.11	0.78	0.87		
3	0.76		−0.91		0.09		0.69			
4a	0.19	0.64	−0.99			0.36	0.63			
5	1.29		−0.55		0.19		0.44		59	
6a	0.58	0.64	−0.61		0.18	0.35	0.38		52	
6b	0.54	0.91	−0.72		0.09	0.07	0.25		26	
6c	0.52	0.76	−0.69	−0.59	0.15	0.23	0.29	0.40	32	56
7	1.11		−0.97	−0.97	0.26		0.52	0.52	73	73
7′	1.10		−0.97		0.26		0.53		74	
7″	1.11		−0.97		0.25		0.52		71	
8a	0.50	0.55	−1.00	−1.01	0.24	0.37	0.46	0.46	65	
8a′	0.52	0.50	−1.00		0.24	0.43	0.48		66	
8a″	0.51	0.61	−1.01		0.23	0.36	0.45		62	
8b	0.41	0.86	−1.16		0.14	0.12	0.34		37	
8c	0.33	0.80	−1.13	−1.00	0.19	0.18	0.39	0.48	36	DB
8c″	0.46	0.73	−1.13	−1.00	0.20	0.22	0.36	0.49	42	68
8ts	0.32	0.71	−1.00	−0.97	0.23	0.28	0.44	0.48	55	59
9	0.84		−1.16		0.33		0.52		85	
9′	0.85		−1.11	−1.05	0.26		0.56	0.70		DB
9″	1.02		−1.13		0.09		0.55			
10a	0.36	0.51	−1.20		0.30	0.49	0.60		76	
10a′	0.51	0.58	−1.27		0.06	0.42	0.46			
10b	0.40	0.77	−1.40		0.04	0.15	0.37			
10b′	0.40	0.72	−1.32		0.22	0.27	0.53		55	
10c	0.28	0.71	−1.36	−1.19		0.25	0.40	0.63		DB

[a] Second-order interaction energy between the boron p_z orbital and a lone pair on X; DB = a double bond was localized by the NBO program. [b] X = central atom of substituent R. [c] Occupancy of the boron p_z orbital.

The boron−lithium bond distance is 2.22 Å. As in the case of lithiodimethylborane (**4a**), this bond has substantial covalent character. The NPA charge on lithium in **6a** is +0.64, while the B−Li bond order is 0.35. The boron−lithium bond NLMO can be considered a boron lone pair (85% localized on boron) with relatively little directionality ($sp^{0.66}$). The higher electronegativity of fluorine, in **6a**, than of methyl groups, in **4a**, causes the negative charge on the F_2B^- fragment to be localized more on the fluorine substituents. The NPA charge on boron is +0.58 (+1.29 in F_2BH), compared to +0.19 in **4a**.

Moving the lithium cation away from the symmetrical position to one of the fluorine substituents, F^1, to form the bridged structure **6c**, causes the boron−lithium bond to become shorter (the B−Li distance is reduced by 0.17 Å to 2.05 Å) and more ionic. The positive NPA charge on lithium in **6c** increases to +0.76, while the covalent contribution to the B−Li bond decreases (the NLMO bond order is 0.23). The loss of covalent bonding in the B−Li bond is compensated by Coulomb attraction between lithium and F^1, the fluorine substituent closest to lithium. F^1 becomes more negatively charged, while the bond B−F^1 is weakened and π donation from F^1 to boron is decreased. The F(1p) → B(p*) delocalization energies indicate that about $^2/_3$ of the electron density in the boron p_z orbital comes from F^2.

The inverted structure **6b** is best described as a contact ion pair. The NPA charges on lithium and fluorine are +0.91 and −0.72, respectively, while covalent B−Li bonding is almost absent; the B−Li NLMO bond order is only 0.07. Instead of a B−Li bond, an almost spherical boron lone pair, with $sp^{0.26}$ hybridization, is localized by the NLMO program. Furthermore, NBO analysis indicates that the stabilization due to π donation from fluorine to boron in **6b** is about half of the delocalization energy in **6a**. The boron p_z occupancy is only 0.09 e. The energetic effect of the loss of B−F π bonding and covalent B−Li bonding is not fully compensated by the increased electrostatic interaction between lithium and fluorine. Hence, **6b** is the least stable isomer.

Dihydroxylithioborane (**8**) prefers a bridged structure, type **C**, in which the hydrogen of the noncoordinating hydroxy group points toward the other oxygen. The additional degrees of freedom associated with the different orientations of the hydroxy groups increase the number of possible structures both for dihydroxylithioborane (**8**) and for dihydroxyborane (**7**), but the *cis,trans* configuration (*i.e.* with one hydroxy group directed toward and one directed away from the third substituent) is most stable. The relative energies of all alternative structures of **8**, including the "inverted" structure **8b**, all lie within the range 4.5−5.8 kcal/mol above the most stable structure **8c**. Note that no "classical" *cis,trans* minimum **8a** exists: even though a structure for **8a**, and a transition structure **8ts** between **8a** and **8c**, can be calculated both at RHF/6-31G* and at MP2/6-31G*, the relative energy of **8ts** is 1.0 kcal/mol *lower* than that of **8a** at MP4/6-311+G**, indicating that **8a** would collapse to **8c**.

Compared to fluorine, the tendency to form a double bond to boron is larger for oxygen, which is a better π donor. Indeed, the occupancy of the boron p_z orbital is larger, between 0.19 for **8c** and 0.24 for the "classical" *cis,cis* conformer **8a′**, and the perturbational interaction energies between the oxygen lone pair and the boron p_z orbital are very large. In the case of **8c**, a strongly B^+O^- polarized π bond instead of a donor−acceptor pair is found by the NBO program for the bond between boron and the noncoordinating oxygen. Compared to *cis,trans*-dihydroxyborane (**7**), this bond is elongated and weakened, but only to a little extent, while the O−B−O angle again is significantly contracted, from 119.3° in **7** to 110.7° in **8c**. The charge distribution in **8c** is similar to that in bridged difluorolithioborane (**6c**). The positive charge on boron is somewhat lower in **8c** than in **6c**, in line with the lower electronegativity of oxygen. The charge on lithium is +0.80, which is only little lower than the values calculated for lithium in organolithium compounds.[4]

As in the case of difluorolithioborane (**6**), the "inverted" structure **8b** has most ion pair character. The NPA charge on lithium is +0.86, and an $sp^{0.39}$ hybridized lone pair is localized on boron. The proximity of the lithium cation polarizes the boron–oxygen (and oxygen–hydrogen) bonds, which leads to a higher negative charge (−1.16) on oxygen. The NLMO bond order, the degree of boron oxygen π bonding, and the occupancy of the boron p_z orbital in **8b** are lowered, compared to **8c**, but only modestly. As a consequence, the resulting loss of bonding energy can largely be compensated by the increased Coulomb attraction between lithium and oxygen and **8b** is only little higher in energy than the most stable isomer **8c**.

Diaminolithioborane (**10**) strongly prefers a planar classical structure, type **A**, in which both nitrogen lone pairs can optimally interact with the boron p_z orbital. The same structural preference is seen for diaminoborane (**9**). Rotation of one of the amino groups leads to the bridged structure **10c**, which is a transition structure, 11.8 kcal/mol less stable than the minimum **10a**. The "classical" structure **10a′**, with both amino groups perpendicular to the plane through the boron and nitrogen atoms, and the two inverted structures **10b′**, all planar, and **10b**, with two amino groups perpendicular, are much higher in energy and have two or more imaginary frequencies; *i.e.* they are not significant as structural candidates for **10** and only serve as comparison structures with B–N donor interaction and/or boron lithium bonding "turned off".

The reason for the difference in conformational preference between diaminolithioborane (**10**) and the dihydroxy derivative **8** is clear: interaction of the lithium cation with the lone pair on nitrogen, as in **10b,c**, makes this lone pair unavailable for π-bonding to boron, while coordination of lithium to oxygen, in **8b,c**, leaves the second oxygen lone pair available for an albeit weakened interaction with the boron p_z orbital. In the planar "inverted" structure **10b′**, boron nitrogen π bonding is possible, but the lithium cation is coordinated "side-on" and cannot interact with the nitrogen lone pairs.

Of all lithioboranes studied here, **10a** has the most covalent lithium boron bond. The charge on lithium in **10a** is only +0.51, and the NLMO bond order is 0.49. The charge on nitrogen increases from −1.16 in **9** to −1.20 in **10a**. Interestingly, the NLMO bond order indicates a significant strengthening of the boron nitrogen bonds in **10a**, relative to **9** (a decrease in bond order is calculated for the boron–fluorine and boron–oxygen bonds; *vide supra*). However, π bonding between boron and nitrogen is weakened upon lithiation, as is indicated by the boron p_z occupancy, which is 10% lower for **10a** than for **9**, by the perturbational donor–acceptor interaction energies, and by the barriers to rotation of the amino groups. For diaminoborane (**9**), rotation of one amino group gives structure **9′**, which is 12.8 kcal/mol higher in energy than **9**. Rotation of an amino group in **10a** leads to the bridging structure **10c**, which is 11.8 kcal/mol less stable than **10a**. These values suggest that the lithium–nitrogen interaction in **10c** is very weak: a strong interaction would stabilize **10c** and lead to a lower rotational barrier. The effect of rotating the amino groups is not additive. The loss of one interaction is compensated by an increase in strength of the other one. Rotation of both amino groups leads to structures **9″** and **10a′**, which are higher in energy by 42.6 and 37.2 kcal/mol, respectively.

In contrast with the bonding situation for the "inverted" structures of difluorolithioborane (**6b**) and dihydroxylithioborane (**8b**), a polarized covalent bond is localized by the NBO program for the boron–lithium bond in **10b** and **10b′**. The NLMO bond order is 0.15 for **10b** and 0.27 for **10b′**, despite the inverted configuration around boron. The hybridization of the corresponding natural hybrid orbital on boron is $sp^{0.53}$ for **10b** and $sp^{0.58}$ for **10b′**. In line with Bent's rule,[13] the lower electronegativity of the substituents in **10**, compared to **6** and **8**, leads to an increase in the directionality of the lone pair or hybrid orbital on boron.

Substituent Effects on Lithioboranes. The effect of the substituents on boron is evaluated using the isodesmic equations:

$$F_2BH + H_2BLi \rightarrow F_2BLi + BH_3 \qquad \Delta E = -7.5 \text{ kcal/mol}$$

$$(HO)_2BH + H_2BLi \rightarrow (HO)_2BLi + BH_3 \qquad \Delta E = -2.4 \text{ kcal/mol}$$

$$(H_2N)_2BH + H_2BLi \rightarrow (H_2N)_2BLi + BH_3 \qquad \Delta E = +5.9 \text{ kcal/mol}$$

$$(H_3C)_2BH + H_2BLi \rightarrow (H_3C)_2BLi + BH_3 \qquad \Delta E = +4.4 \text{ kcal/mol}$$

Two substituent effects are important. First, electronegative substituents lower the electron density on boron and hence stabilize the lithioborane. The amino substituent clearly deviates from this trend, due to the second substituent effect. Diaminoborane is stabilized due to π donation to boron by the amino groups. Lithiation on boron counteracts π donation, which thus destabilizes the lithioborane.

Addition of Lithioboranes to Formaldehyde. Although lithioboranes are moderately polar compounds, the charge distribution in the anionic moiety is distinctly different from that found e.g. in alkyllithiums. No "umpolung" on boron occurs. The boron atom bears a positive charge (the parent compound H_2BLi (**2**) is an exception). Are these compounds able to react as nucleophiles? To answer this question, we have studied a typical model nucleophilic reaction, the addition to formaldehyde (**11**) of three lithiated boranes, H_2BLi (**2**), $(CH_3)_2BLi$ (**4**), and F_2BLi (**6**). Interestingly, the results are very similar to the corresponding reaction of monomeric methyllithium with formaldehyde.[14]

Tables 5 and 6 list absolute and relative energies, and geometries are shown in Figures 2 and 3.

The first stage of the reaction is the formation of a precursor complex, in which the carbonyl oxygen is coordinated side-on to lithium. These complexes are highly flexible structures, with the formaldehyde moiety, lithium, and boron approximately in a plane. Complexation energies, at MP2(fc)/6-31+G* + ΔZPE, are −15.1 kcal/mol for complex **12** of formaldehyde and lithioborane (MP4/6-311+G**: −19.6 kcal/mol), −14.4 kcal/mol for the lithiodimethylborane formaldehyde complex **16**, and −18.4 kcal/mol for **19**, the complex of difluorolithioborane and formaldehyde. These values do not differ significantly from the complexation energy of −16.4 kcal/mol for the methyllithium formaldehyde complex (MP4/6-31+G**).[14b]

Alternatively, coordination of the carbonyl oxygen to boron, or both to boron and lithium, might be possible. However, coordination to boron is generally weaker than coordination to lithium. At MP4/6-311+G**, the complexation energy of borane and formaldehyde, in complex **15**, is −15.9 kcal/mol.[15] As expected on the basis of this result, we were unable to locate minima with the carbonyl oxygen coordinated to boron or both to boron and lithium. Upon optimization, the structures changed to those of the lithium coordinated complexes.

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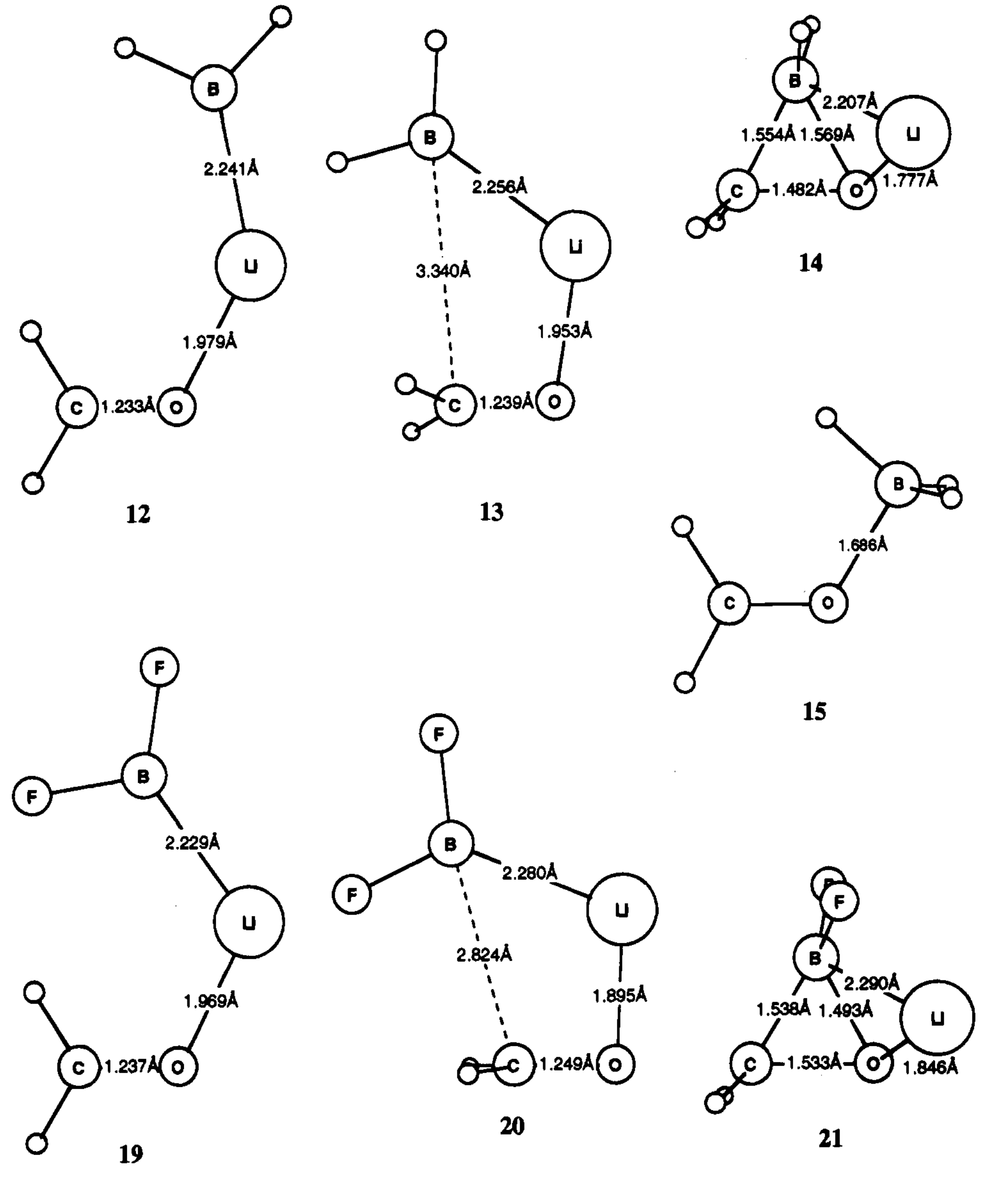
(14) (a) Kaufmann, E.; Schleyer, P. v. R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560. (b) van Eikema Hommes, N. J. R.; Schleyer, P. v. R. Manuscript in preparation.

(15) LePage, T. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 6642.



12 **13** **14** **15** **19** **20** **21**

Figure 2.

Table 5. Absolute Energies (au) and Zero Point Vibrational Energies (kcal/mol) for the Reaction $HC_2C{=}O$ + $LiBR_2$ (R = H, CH_3, F)

struct	point group	HF/6-31G*	ZPE//6-31G*	MP2/(fu)/6-31G*	MP2(fc)/6-31+G*	MP4(fc)/6-311+G**
11	C_{2v}	−113.866 33	18.33(0)	−114.171 96	−114.177 08	−114.261 98
11 + 2a		−147.076 27	30.05	−147.469 05	−147.471 73	−147.608 15
12	C_s	−147.106 19	31.54(0)		−147.497 86	−147.641 48
13	C_1	−147.098 08	32.24(1)		−147.492 02	−147.636 61
14	C_1	−147.199 87	35.77(0)		−147.620 76	−147.755 91
11 + 1		140.256 34	35.71	−140.640 53	−140.637 44	−140.780 24
15	C_s	−140.268 02	39.96(0)	−140.669 61	−140.665 11	−140.811 66
11 + 4a		−225.168 58	69.08	−225.837 86	−225.834 76	
16	C_1	−225.197 45	70.44(0)	−225.870 70	−225.859 68	
17	C_1	−225.188 00	71.05(1)	−225.863 80	−225.854 12	
18	C_1	−225.287 98	73.41(0)	−225.989 61	−225.978 16	
11 + 6a		−344.955 69	24.12	−345.698 06	−345.718 73	
19	C_s	−344.989 51	25.59(0)	−345.735 70	−345.750 12	
20	C_s	−344.975 84	26.54(1)	−345.729 07	−345.742 09	
21	C_1	−345.076 91	28.29(0)	−345.843 05	−345.847 04	

All these reactions are very exothermic. Relative to the precursor complexes, the reaction energies, at MP2(fc)/6-31+G* + ΔZPE, are −73.3 kcal/mol for the H_2BLi addition leading to product **14** (MP4/6-311+G**: −68.0 kcal/mol), −71.6 kcal/mol for $(CH_3)_2BLi$ giving **18**, and −58.4 kcal/mol for F_2BLi to give **21**. These products have an interesting three-membered B−C−O ring structure, with a dative boron−oxygen bond. The lithium cation occupies a bridging position over the boron oxygen bond and interacts with one of the substituents on boron. Addition of methyllithium to formaldehyde is less exothermic, 43.5 kcal/mol relative to the precursor complex.[14b]

As in the case for the addition of methyllithium, the transition structures **13**, **17**, and **20** for the addition to the formaldehyde carbonyl bond all occur early on the reaction coordinate. The carbon−oxygen bonds are elongated to a small extent, but this is due to the stronger interaction with lithium rather than to the

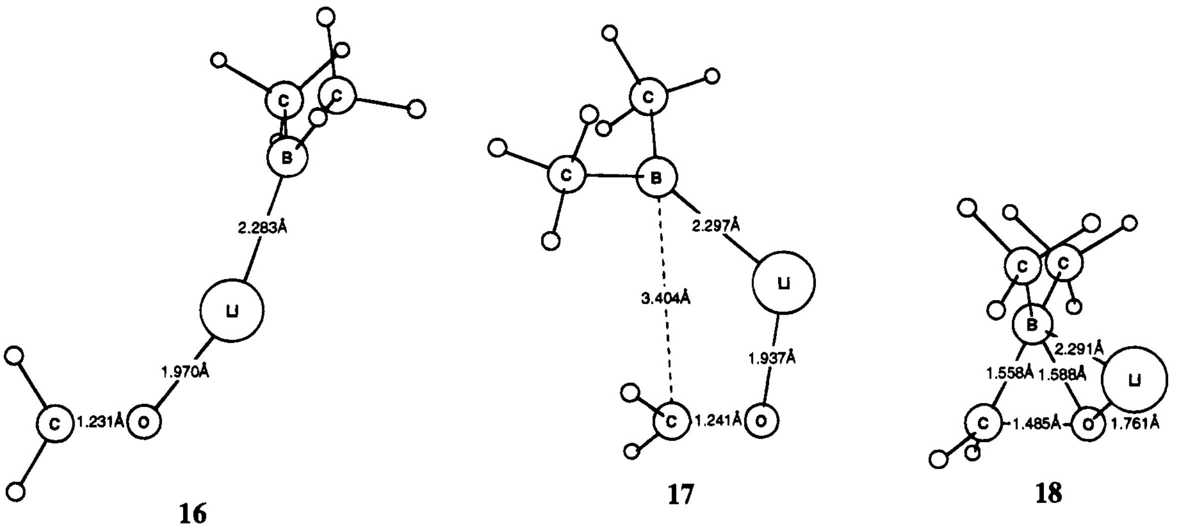


Figure 3.

Table 6. Relative Energies (kcal/mol) for the reaction $H_2C{=}O + LiBR_2$ (R = H, CH_3, F)[a]

struct	HF/6-31G*	MP2(fu)/6-31G*	MP2(fc)/6-31+G*	MP4(fc)/6-311+G**	MP2(fc) incl ΔZPE//6-31G*	MP4 incl ΔZPE//6-31G*
11 + 2a	18.78		16.40	20.91	15.1	19.6
12	0.00		0.00	0.00	0.0	0.0
13	5.09		3.66	3.06	4.3	3.7
14	−58.79		−77.12	−71.81	−73.3	−68.0
11 + 1	7.33	18.25	17.36	19.72	13.5	15.9
15	0.00	0.00	0.00	0.00	0.0	0.0
11 + 4a	18.12	20.61	15.64		14.4	
16	0.00	0.00	0.00		0.0	
17	5.94	4.33	3.49		4.1	
18	−56.81	−74.62	−74.35		−71.6	
11 + 6a	21.22	23.62	19.70		18.4	
19	0.00	0.00	0.00		0.0	
20	8.58	4.16	5.04		5.9	
21	−54.84	−67.36	−60.82		−58.4	

attack of boron to the carbonly carbon. The carbon−boron distance (H_2BLi, 3.34 Å, $(CH_3)_2BLi$, 3.40 Å; F_2BLi, 2.82 Å) is much longer than a carbon−boron bond, so that a weak interaction can be expected at best. The activation barriers (values: MP2(fc)/6-31+G* + ΔZPE) are low, 4.3 kcal/mol for the addition of H_2BLi via **13** (MP4/6-311+G**: 3.7 kcal/mol), 4.1 kcal/mol for addition of $(CH_3)_2BLi$ via **17**, and 5.9 kcal/mol for reaction of F_2BLi, via transition structure **20**. The barrier for methyllithium addition is still somewhat lower, 2.6 kcal/mol.

Do these transition structures indeed correspond to the addition of a lithioborane to the carbonyl double bond? Alternatively, attack of the negatively charged substituents instead of the positively charged boron might be conceivable. However, this possibility appears unlikely in view of the geometry of the transition structure, as can be clearly seen in **17**, for the addition of $(CH_3)_2BLi$. In the precursor complex **16**, the carbonyl CH_2 group is in the plane of the molecule, while, in the product **18**, the hydrogens are out of the BCO plane. Rotation of the CH_2 group takes place upon attack, but the hydrogen pointing upward, to the boryl anion moiety, in **16** moves in the direction of the closest methyl substituent on boron. In the transition structure **17**, this hydrogen points toward the methyl substituent, and an interaction between the methyl group and the p orbital of the carbonyl carbon, expected in the case of attack of the methyl group, is not possible.

Conclusions

Lithioboranes are moderately polar compounds, with a significant covalency in the lithium−boron bond. With the exception of the parent compound lithioborane, the boron atom remains positively charged and the partial negative charge of the boryl anion moiety is located on the boron substituents. Hence, lithioboranes are stabilized by electronegative substituents. Lithiation at boron weakens π bonding between boron and the substituents. The addition reaction of lithioboranes to formaldehyde is computed to proceed similar to the addition of methyllithium. Lithioboranes have interesting potential as nucleophilic reagents.

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