Skeletally Stabilized Diborylamines: *N*-Boryl and *N*-Silyl Derivatives of the 1,3,2-Diazaboracylcohexane Ring System

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The parent 1,3,2-diazaboracyclohexane ring systems c-N(H)B(R)N(H)C_3H_6 (**1–4**: R = Ph, Me, *i*-Pr, *t*-Bu) were converted to a series of mono- and disilyl derivatives c-N(E)B(R)N(X)C_3H_6 (**5–8**: E = $SiMe_3$; X = H; R = Ph; Me, *i*-Pr, *t*-Bu. **9–11**: E = X = $SiMe_3$; R = Ph, Me, *i*-Pr. **12, 13**: E = *t*-$BuMe_2Si$; X = H, $SiMe_3$; R = Ph) by deprotonation with *n*-BuLi followed by addition of Me_3SiCl or *t*-$BuMe_2SiCl$. Deprotonation/substitution reactions with chloroboranes, rather than chlorosilanes, afforded several *N*-boryl derivatives of the Ph–B (**1**) ring system [**14, 15**: E = H; X = $B(NMe_2)_2$, B(Ph)NMe_2. **16, 17**: E = $SiMe_3$; X = $B(NMe_2)_2$, B(Ph)NMe_2. **18**: E = X = $B(BNMe_2)_2$]. Silicon–nitrogen bond cleavage reactions of the N–$SiMe_3$ compounds **5** and **9** with $PhBCl_2$ gave the thermally unstable **B–Cl** derivatives **19, 20** [E = H, $SiMe_3$; X = B(Ph)Cl] which, in turn, were converted to the B–NMe_2 analogs **15** and **17** by reactions with Me_3SiNMe_2. The more sterically congested diborylamines **12–26** [R = *i*-Pr, *t*-Bu; E = H, $SiMe_3$; X = $B(NMe_2)_2$, B(Ph)NMe_2, B(Ph)OCH_2CF_3], were prepared from **3**, **4**, or **7** by similar methods or by dehydrohalogenation reactions. A selective Si–N cleavage reaction of the unsymmetrical disilyl ring system **13** with $PhBCl_2$ afforded the more stable **B–Cl** derivative **27** [E = *t*-$BuMe_2Si$; X = B(Ph)Cl]. These new compounds were characterized by multinuclear NMR spectroscopy and elemental analyses. In some cases (**15, 17, 18**), barriers to rotation about the terminal B–NMe_2 bonds were determined by dynamic ^1H NMR spectroscopy.

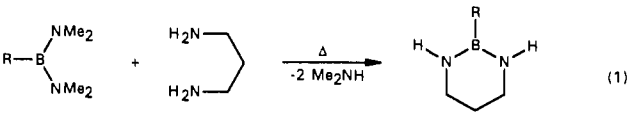
Introduction

The current high level of interest in boron–nitrogen compounds stems mainly from their potential as precursors to B–N polymers, BN-based ceramics, and other solid-state materials.[1] *Linear* B–N polymers [i.e., poly(iminoboranes),[2] $(RBNR)_n$] are especially intriguing since they are not only preceramic polymers[3] but they are also the isoelectronic analogs of polyacetylene and related conducting materials. Unfortunately, most potential synthetic routes to B–N polymers are thwarted by the very high thermal stability of the cyclic trimers [i.e., borazines $(RBNR)_3$].[4] In order to circumvent the problem of ring formation, we are exploring two different synthetic approaches, both involving diborylamines as possible condensation monomers. The incorporation of a linear B–N–B–N unit along with other structural features is intended to prevent these systems from thermally condensing to the six-membered borazine rings. In the first method, acyclic diborylamines that contain both Si–N and B–X functional groups are the starting materials. A few such compounds, utilizing the sterically protecting *t*-Bu group on boron, have been reported earlier.[5]

This study is related to the second synthetic approach which involves the "skeletal stabilization" [6] of the N–B–N–B backbone through bridging $-(CH_2)_3-$ units by use of the 1,3,2-diazaboracyclohexane ring system (e.g., **1–4**, eq 1). By providing some degree of structural rigidity, the trimethylene bridges are intended to prevent the B–N backbone from condensing to the cyclic trimer. Specifically, we report here the synthesis and characterization of a variety of new *N*-silyl and *N*-boryl derivatives of the 1,3,2-diazaboracyclohexane ring system. Depending on the particular substituents attached to the ring, these compounds are of interest as potential B–N polymer precursors, as structural and/or stereochemical models for the linear B–N backbone,[7] or as reagents for the preparation of other novel B–N–element (e.g., B–N–P)[8] derivatives.

Results and Discussion

Starting Materials and *N*-Silyl Derivatives. A series of 1,3,2-diazaboracyclohexanes, used as starting materials in this study, were prepared by the transamination reaction (eq 1) as reported



(1)

1: R = Ph 3: R = *i*-Pr
2: R = Me 4: R = *t*-Bu

by Niedenzu.[9] While the *B*-phenyl (**1**) and -methyl (**2**) derivatives are known compounds,[9] the more sterically crowded analogs **3** and **4** do not appear to have been previously reported. These new compounds were obtained in good yields as thermally stable, distillable liquids and were fully characterized by NMR spectroscopy (^1H, ^{13}C, and ^{11}B) and elemental analysis (Tables 1 and 2). Compounds **3** and **4** were of interest in order to assess the effect of steric hindrance on the subsequent derivative chemistry of the ring system and on the thermal stability of the resulting products.

In the initial phase of this study, we prepared both the monosilyl (**5–8**) and the disilyl (**9–11**) derivatives of the diazaboracyclohexane ring systems by means of stepwise deprotonation/substitution reactions (eqs 2 and 3). Generally, these reactions

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(1) See the following general review and references cited therein: Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73.
(2) For the synthesis and structures of the *monomeric* and *dimeric* iminoboranes, see: Paetzold, P.; von Plotho, C. *Chem. Ber.* **1982**, *115*, 2819.
(3) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297.
(4) For an early review, see: Atkinson, I. B.; Currell, B. R. *Inorg. Macromol. Rev.* **1971**, *1*, 203.
(5) Li, B.-L.; Neilson, R. H. *Inorg. Chem.* **1986**, *25*, 361.
(6) This concept has also been applied to P–N systems as well. For a leading reference, see: Barendt, J. M.; Haltiwanger, R. C.; Squier, C. A.; Norman, A. D. *Inorg. Chem.* **1992**, *30*, 2342.
(7) Shaw, S. Y.; DuBois, D. A.; Watson, W. H.; Neilson, R. H. *Inorg. Chem.* **1988**, *27*, 974.
(8) Shaw, Y. S.; Scheide, G. M.; Davis, C. E.; Mukherjee, P.; Neilson, R. H. *Phosphorus, Sulfur and Silicon Relat. Elem.* **1989**, *41*, 141.
(9) Niedenzu, K.; Fritz, P.; Dawson, J. W. *Inorg. Chem.* **1964**, *3*, 361.

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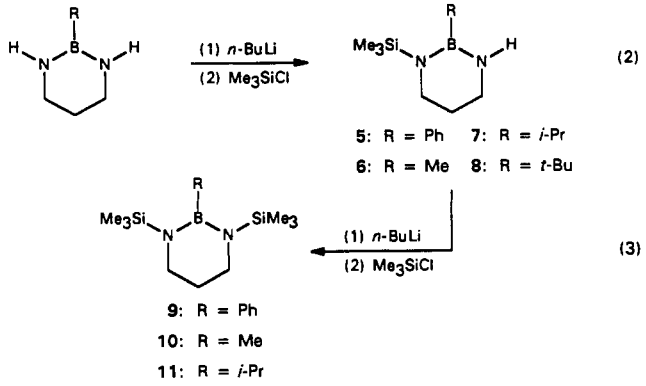


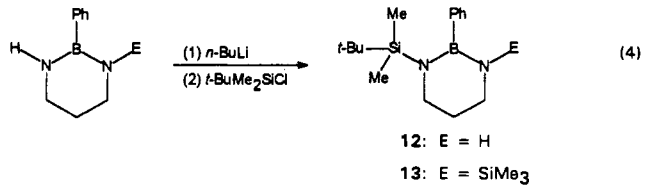
(2)

(3)

proceeded smoothly and the products **5–11** were obtained in yields of ca. 50–80% as colorless, thermally stable liquids (or as a low-melting solid in the case of **9**). The NMR spectral data (Table 1) for these compounds are completely consistent with the proposed structures. The observation of nonequivalent N–CH_2 groups in the ^{13}C NMR spectra of the unsymmetrical derivatives **5–8** and the integrated intensities of the Me_3Si and $-(CH_2)_3-$ signals in the ^1H NMR spectra are particularly diagnostic.

The optimum experimental conditions for these reactions varied considerably with the steric bulk of the substituent on boron. Thus, while the phenyl- (**1** and **5**) and the methyl-substituted rings (**2** and **6**) were readily deprotonated by *n*-BuLi (in THF solution at 0 °C), the more hindered isopropyl (**3** and **7**) and *t*-butyl (**4** and **8**) analogs required the addition of 1 equiv of TMEDA (in hexane solution at reflux) to ensure complete lithiation. The relative rates of the reactions of the intermediate *N*-lithio derivatives with Me_3SiCl also decreased markedly with increasing steric bulk of the group on boron to the point where the disilyl derivative of the *tert*-butyl ring system (**8**) could not be prepared.

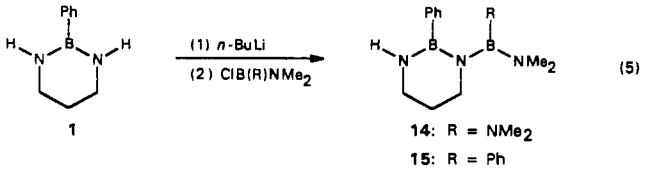
The effect of steric hindrance at the *N*-silyl center was also investigated to some extent. Treatment of *N*-lithio derivatives of the B–Ph ring systems (**1** and **5**) with *tert*-butyldimethylchlorosilane afforded compounds **12** and **13** (eq 4) in ca. 80% yield. Again, the unsymmetrical structure is confirmed by the NMR, especially ^{13}C, spectral data.



(4)

***N*-Boryl Derivatives of the B–Ph Ring Systems.** In this study, a variety of *N*-boryl derivatives of the 1,3,2-diazaboracyclohexane ring system were prepared by three different synthetic routes: (1) deprotonation/substitution reaction of the N–H bonds, (2) cleavage of *N*-silyl side groups by chloroboranes, and (3) dehydrohalogenation reactions of the N–H bonds with chloroboranes.

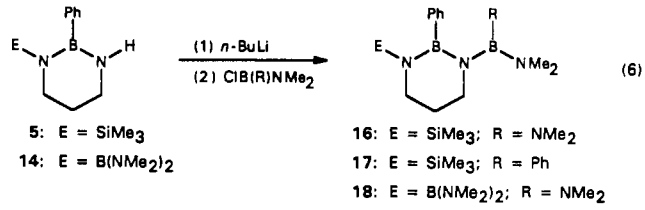
The first approach was found to be most effective in the case of the *B*-phenyl rings. Thus, addition of the chloroboranes ClB(R)NMe_2 (R = NMe_2, Ph) to an ether solution of the *N*-lithio derivative of **1** (eq 5) afforded diborylamines **14** and **15**,



(5)

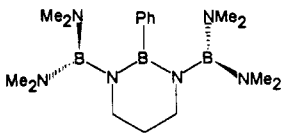
respectively. *Unlike many of their acyclic counterparts*[10] *that often decompose readily to borazines, these diborylamines are thermally stable, distillable liquids.* Their enhanced thermal stability is most likely due to the "skeletal *stabilization*" provided by the bridging $-(CH_2)_3-$ linkage that helps to prevent rearrangement of the linear B–N framework to a six-membered B–N ring system.

Application of the same reaction sequence to the monosubstituted rings (e.g., **5** and **14**) gave the mixed *N*-silyl/*N*-boryl derivatives **16** and **17** as well as the symmetrical bis(boryl) analog **18** (eq 6).



(6)

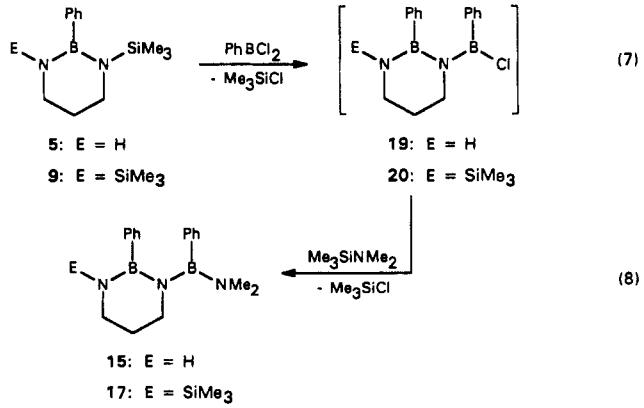
As noted in a preliminary account,[7] compound **18** is significant since it contains a *linear* backbone of six B–N bonds and, as such, is a useful structural model for a linear B–N polymer. Interest-



18

ingly, both X-ray diffraction and variable-temperature NMR studies of **18** indicate that the exocyclic $B(NMe_2)_2$ groups are rotated out of the plane of the BN_2C_3 ring. The rotation barrier (ΔG^*) about the B–NMe_2 bonds in **18** was found to be 12.9 kcal/mol,[11] as compared to the much higher values of 17.3 and 18.4 for the $-B(Ph)NMe_2$ derivatives **15** and **17**, respectively. These structural and stereochemical data indicate a substantial degree of (p–p)π overlap in the terminal B–NMe_2 bonds but a significantly weaker π interaction between the ring nitrogen atoms and the pendant boryl groups due to the "twisted" orientation of the side groups.

The second synthetic method (i.e., Si–N bond cleavage) was employed in attempts to prepare the chloroboryl derivatives **19** and **20** (eq 7). The *N*-silyl compounds **5** and **9** reacted smoothly



(7)

(8)

with $PhBCl_2$ at 0 °C in CH_2Cl_2 solution to yield these highly reactive and thermally unstable B–Cl species. Upon solvent

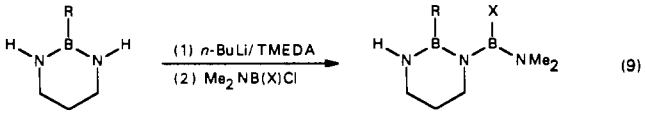
(10) See, for example: (a) Gasparis, T.; Nöth, H.; Storch, W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 326. (b) Storch, W.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 235. (c) Nöth, H.; Storch, W. *Chem. Ber.* **1976**, *109*, 884.

(11) Boron–nitrogen rotation barriers were determined by the "coalescence-temperature" method. See for example: Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1977**, *16*, 7.

removal, **19** decomposed into an uncharacterized solid residue, probably via HCl elimination, as is typical of compounds containing both N–H and B–Cl bonds.[5] Compound **20**, which was isolated as an opaque yellow gum, was somewhat more stable. The NMR spectral data (Table 1) obtained for this material are consistent with the proposed structure. Most notable is the observation of two distinct signals in the ^{11}B NMR spectrum at 36.7 and 45.4 ppm.

Chemical evidence for the formation of these B–Cl derivatives comes from their rapid reaction with Me_3SiNMe_2 to afford the stable B–NMe_2 analogs **15** and **17** (eq 8). The NMR spectral data and physical properties of these products were identical to those of the same compounds prepared by the deprotonation/substitution sequence (eqs 5 and 6).

***N*-Boryl Derivatives of the *i*-Pr–B and *t*-Bu–B Ring Systems.** Since some of the more highly functionalized derivatives (e.g., the B–Cl systems **19** and **20**) of the *B*-phenyl ring system were not very stable, we began to focus instead on the more hinered *i*-Pr and *t*-Bu analogs. As mentioned above, the deprotonation/substitution reactions of these hindered rings required the use of TMEDA to promote the process. For example, treatment of the *N*-lithio derivatives of **3** and **4** with monochloroboranes afforded the diborylamines **21–23** (eq 9). Like their *B*-phenyl analogs, these new compounds were obtained as fully characterized, thermally stable, distillable liquids.

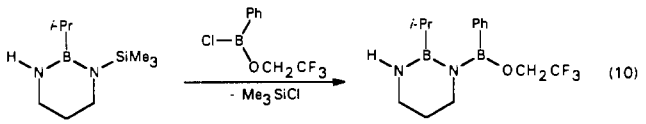


(9)

3: R = *i*-Pr
4: R = *t*-Bu

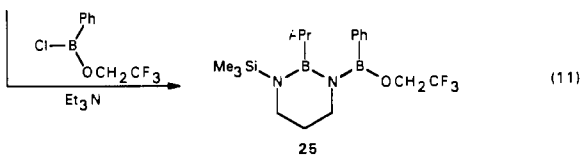
21: R = *i*-Pr, X = NMe_2
22: R = *i*-Pr, X = Ph
23: R = *t*-Bu, X = NMe_2

With these bulky groups on boron, it was not possible to further derivatize the *N*-silyl compounds **7** and **8** by the deprotonation/substitution sequence. Some success, however, was achieved with the other two synthetic methods. For example, the novel phenyl(trifluoroethoxy)boryl derivatives **24** and **25** were obtained from the Si–N bond cleavage (eq 9) and dehydrohalogenation (eq 10),



(10)

7 **24**

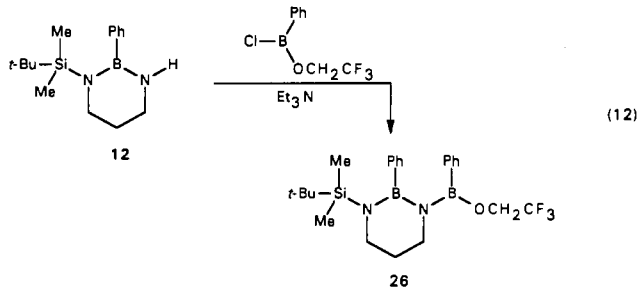


(11)

25

respectively, of the *i*-Pr ring system **7**. The presence of the OCH_2CF_3 substituents in these compounds was confirmed by the observation of the expected quartet resonances (due to ^{19}F coupling) for the CH_2CF_3 moiety in the ^1H and ^{13}C NMR spectra. Unfortunately, we were not able to obtain the corresponding chloroboryl derivatives by using $PhBCl_2$ in place of PhB(Cl)OCH_2CF_3 in either type of reaction. Complex, inseparable mixtures of products were invariably obtained in these attempts.

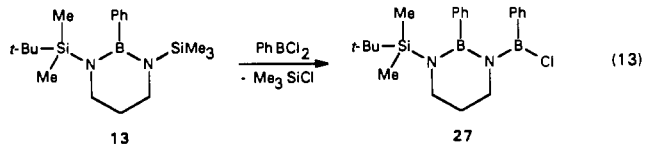
***N*-Boryl Derivatives of the N–$SiMe_2$(*t*-Bu) Ring Systems.** Finally, we studied a few examples of similar reactions of the *N*-(*tert*-butyldimethylsilyl)-*B*-phenyl-substituted 1,3,2-diazaboracyclohexane systems **12** and **13**. When the *N*-lithio derivative of compound **12** was treated with chloroboranes, no reaction occurred, presumably due to steric congestion. On the other hand, the dehydrohalogenation reaction of **12** with the chloro(trifluoroethoxy)borane (eq 12) did afford the desired diborylamine product **26**, albeit in relatively low yield (Tables 1 and 2).



(12)

12 **26**

With the unsymmetrical *N*,*N*-disilyl ring system **13**, the Si–N bond cleavage reaction (eq 13) proceeded smoothly and regioselectively to give the chloroboryl deriative **27** is essentially



(13)

13 **27**

quantitative yield. Although compound **27** underwent decomposition on attempted distillation, it was fully characterized by NMR spectroscopy *and elemental analysis* prior to distillation. Both the ^1H and ^{13}C NMR spectral data (Table 1) indicate the complete absence of any Me_3Si signals, thus confirming the highly selective nature of this reaction. The characteristic downfield signal (ca. 45 ppm) of the –B(Ph)Cl center is clearly observed in the ^{11}B NMR spectrum in addition to the signal (ca. 39 ppm) of the ring boron atom.

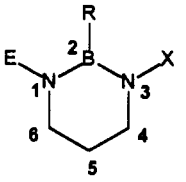
Conclusion. This work clearly demonstrates that a wide variety of *N*-silyl and/or *N*-boryl derivatives of the 1,3,2-diazaboracyclohexane ring system can be readily prepared. The *N*-boryl compounds, especially the bis(boryl) analog **18**, are of interest as model compounds for a linear B–N polymer system. More importantly, the difunctional *N*-boryl derivatives, notably **21–27**, are potential condensation "monomers" for the ultimate preparation of new B–N polymers and ceramic materials. The thermal decomposition reactions of several of these compounds will be discussed in a future publication.

Experimental Sections

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: Me_3SiCl, Me_3SiNMe_2, *n*-BuLi (hexane solution), *t*-BuLi (pentane solution), *i*-PrMgCl (THF solution), and $H_2N(CH_2)_3NH_2$. Hexane, ether, CH_2Cl_2, Et_3N, and TMEDA were distilled from CaH_2 and stored over molecular sieves. The following reagents were prepared according to published procedures: $PhBCl_2$,[12] $(Me_2N)B(R)Cl$ (R = Me_2N, Ph),[13] $PhB(NMe_2)_2$,[13] $CF_3CH_2OB(Ph)Cl$,[14] and *t*-$BuMe_2SiCl$.[15] The alkylboranes, $(Me_2N)_2BR$ (R = Me, *i*-Pr, *t*-Bu), were prepared respectively by addition of MeMgBr (2.0 M in ether), *i*-PrMgCl (2.0 M in THF), or *t*-BuLi (1.6 M in pentane) to an equimolar amount of $(Me_2N)_2BCl$ in ether (ca. 1 M solution) at 0 °C. The 1,3,2-diazaboracyclohexanes **1–4** were prepared by the transamination reaction of $H_2N(CH_2)_3NH_2$ with $RB(NMe_2)_2$ according to the published procedure.[9] Characterization data for the new compounds **3** and **4** are summarized in Tables 1 and 2. Proton, ^{13}C, and ^{11}B NMR spectra were recorded on a Varian XL-300 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or

(12) Jolly, W. L. *The Synthesis and Characterization of Inorganic Compounds*; Prentice-Hall: Englewood Cliffs, NJ, 1970; p 481.
(13) Niedenzu, K.; Dawson, J. W. Boron-Nitrogen Compounds; Springer-Verlag: New York, 1965. See also ref 5.
(14) Shaw, S. Y.; Neilson, R. H. *Inorg. Chem.* **1991**, *30*, 148.
(15) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

Table 1. NMR Spectroscopic Data[a] for New 1,3,2-Diazaboracyclohexane Derivatives



compound		NMR				
			^{1}H		^{13}C	^{11}B
		signal	δ	J_{HH}, Hz	δ	δ
3	R = *i*-Pr	*Me*$_2$CH	0.83[b]		19.69	31.6
	E = H	Me$_2$*CH*	1.58	7.1		
	X = H	**4, 6**	3.0–3.1[c]		39.76	
		5	1.71	5.6	27.75	
		NH	2.62			
4	R = *t*-Bu	*Me*$_3$C	0.80		28.62	32.3
	E = H	**4, 6**	3.0–3.1[c]		39.80	
	X = H	**5**	1.72	5.6	27.59	
		NH	2.65			
5	R = Ph	Me$_3$Si	–0.36		1.36	31.3
	E = H	**4, 6**	3.09	5.3	40.30, 42.70	
	X = SiMe$_3$	**5**	1.84	5.5	28.47	
		Ph	7.3–7.4[c]		127–132[c]	
6	R = Me	Me$_3$Si	0.12		1.68	31.5
	E = H	MeB	0.10			
	X = SiMe$_3$	**4, 6**	3.0–3.1[c]		40.08, 42.51	
		5	1.7–1.8[c]		28.54	
7	R = *i*-Pr	Me$_3$Si	0.14		1.99	33.9
	E = H	*Me*$_2$CH	0.86	7.0	20.77	
	X = SiMe$_3$	Me$_2$*CH*	1.13	7.1		
		4, 6	2.9–3.0[c]		39.97, 42.88	
		5	1.68	5.7	28.74	
8	R = *t*-Bu	Me$_3$Si	0.17		3.42	35.2
	E = H	*Me*$_3$C	0.88		30.06	
	X = SiMe$_3$	**4, 6**	2.96	5.7	40.26, 44.05	
		5	1.64	5.7	28.63	
9	R = Ph	Me$_3$Si	–0.22		1.56	33.0
	E = SiMe$_3$	**4, 6**	3.07	5.7	43.15	
	X = SiMe$_3$	**5**	1.84	5.7	29.60	
		Ph	7.2–7.3[c]		127–134[c]	
10	R = Me	Me$_3$Si	0.15		2.22	33.9
	E = SiMe$_3$	MeB	0.29			
	X = SiMe$_3$	**4, 6**	2.93	5.8	43.50	
		5	1.67	5.9	29.80	
11	R = *i*-Pr	Me$_3$Si	0.19		3.04	37.0
	E = SiMe$_3$	*Me*$_2$CH	1.00	7.5	19.92	
	X = SiMe$_3$	Me$_2$*CH*	1.37	7.6		
		4, 6	2.92	5.7	44.16	
		5	1.63	5.7	30.12	
12	R = Ph	Me$_2$Si	–0.23		–2.92	31.8
	E = H	*Me*$_3$C	0.96		27.73	
	X = *t*-BuMe$_2$Si	Me$_3$*C*			19.97	
		4	3.23	5.3	44.00	
		6	3.1–3.2[c]		40.32	
		5	1.89	5.6	28.27	
		NH	3.05			
		Ph	7.3–7.4[c]		127–132[c]	
13	R = *t*-Bu	Me$_3$Si	–0.31		1.55	33.6
	E = SiMe$_3$	Me$_2$Si	–0.44		–2.92	
	X = *t*-BuMe$_2$Si	*Me*$_3$C	0.82		27.96	
		Me$_3$*C*			20.15	
		4	3.06	5.3	44.23	
		6	3.00	5.9	43.76	
		5	1.77	5.6	29.54	
		Ph	7.1–7.3[c]		127–134[c]	
14	R = Ph	**4**	3.2–3.3[c]		43.62	29.7
	E = H	**6**	3.08	5.4	40.84	
	X = B(NMe$_2$)$_2$	**5**	1.89	5.4	28.21	
		NH	2.42			
15	R = Ph	**4**	3.2–3.3[c]		45.03	31.7
	E = H	**6**	3.02	5.4	40.67	36.1
	X = B(Ph)NMe$_2$	**5**	1.86	5.6	28.18	
		NMe$_2$	2.18, 2.46[d]		40.05, 40.10[d]	
		Ph	7.3–7.4[c]		127–132[c]	
16	R = Ph	Me$_3$Si	–0.12		3.93	29.1
	E = SiMe$_3$	**4**	3.16	5.7	46.10	32.1

Table 1 (Continued)

compound		NMR				
			^{1}H		^{13}C	^{11}B
		signal	δ	J_{HH}, Hz	δ	δ
16	X = $B(NMe_2)_2$	**6**	3.00	5.5	45.59	
		5	1.89	5.6	31.48	
		NMe_2	2.36		41.51	
		Ph	7.2–7.3[c]		129–135[c]	
17	R = Ph	Me_3Si	–0.16		1.62	32.7
	E = $SiMe_3$	**4**	3.13	5.9	44.59	35.3
	X = $B(Ph)NMe_2$	**6**	2.94	5.3	43.76	
		5	1.87	5.6	29.20	
		NMe_2	2.40, 2.43[d]		40.00	
		Ph	7.1–7.4[c]		126–134[c]	
18	R = Ph	**4, 6**	3.01	5.4	44.09	29.3
	E = $B(NMe_2)_2$	**5**	1.83	5.4	28.66	31.0
	X = $B(NMe_2)_2$	NMe_2	2.32		39.28	
		Ph	7.1–7.3[c]		126–132[c]	
20	R = Ph	Me_3Si	–0.14		1.56	36.7
	E = $SiMe_3$	**4**	3.71	5.9	45.88	45.4
	X = B(Ph)Cl	**6**	3.20	5.9	43.46	
		5	2.02	5.9	28.95	
		Ph	6.9–7.3[c]		127–134[c]	
21	R = *i*-Pr	Me_2CH	0.80[b]		20.37	33.2
	E = H	Me_2CH	[e]			29.2
	X = $B(NMe_2)_2$	**4**	3.0–3.1[c]		43.38	
		6	2.8–2.9[c]		40.46	
		5	1.7–1.8[c]		28.20	
		NMe_2	2.57		39.53	
22	R = *i*-Pr	Me_2CH	0.86	5.5	20.59	36.0
	E = H	Me_2CH	0.80	5.2		34.0
	X = $B(Ph)NMe_2$	**4**	3.0–3.1[c]		44.79	
		6	2.8–2.9[c]		40.46	
		5	1.77	5.6	28.28	
		NMe_2	2.81, 2.89[d]		40.32	
		NH	3.03			
		Ph	7.4–7.6[c]		127–134[c]	
23	R = *t*-Bu	Me_3C	0.78		29.34	29.2
	E = H	**4**	2.80	5.4	43.94	33.0
	X = $B(NMe_2)_2$	**6**	3.0–3.1[c]		40.53	
		5	1.73	5.6	27.99	
		NMe_2	2.59		39.61	
		NH	2.88			
24	R = *i*-Pr	Me_2CH	0.71	7.1	20.22	32.4
	E = H	Me_2CH	1.36	7.1		35.5
	X = $B(Ph)OCH_2CF_3$	**4**	3.20	2.7	43.50	
		6	3.06	3.0	40.24	
		5	1.75	3.0	27.94	
		OCH_2	3.98	[8.7][f]	64.08 [35.1][g]	
		CF_3			[h]	
		Ph	7.3–7.5[c]		128–132[c]	
25	R = *i*-Pr	Me_3Si	0.21		2.25	35.5
	E = $SiMe_3$	Me_2CH	0.78	7.3	19.58	40.4
	X = $B(Ph)OCH_2CF_3$	Me_2CH	1.36	7.3		
		4, 6	2.96	6.1	42.81, 43.04	
		5	1.67	6.1	29.25	
		OCH_2	4.08	[8.7][f]	63.96 [35.3][g]	
		CF_3			124.32 [278.4][g]	
		Ph	7.3–7.4[c]		128–133[c]	
26	R = Ph	Me_2Si	–0.40		–2.61	36.6
	E = *t*-$BuMe_2Si$	Me_3C	0.87		27.93	
	X = $B(Ph)OCH_2CF_3$	Me_3C			19.88	
		4	3.15	5.4	43.04	
		6	3.36	6.0	44.42	
		5	1.85	5.8	28.95	
		OCH_2	3.67	[8.7][f]	63.77 [35.1][g]	
		CF_3			[h]	
		Ph	6.8–7.2[c]		126–133[c]	
27	R = Ph	Me_2Si	–0.29		–2.63	38.6
	E = *t*-$BuMe_2Si$	Me_3C	0.97		27.82	45.0
	X = B(Ph)Cl	Me_3C			19.66	
		4	3.69	6.7	45.07	
		6	3.26	5.5	43.73	
		5	1.96	6.1	28.97	
		Ph	6.8–7.1[c]		126–134[c]	

[a] Proton and ^{13}C chemical shifts downfield from Me_4Si, ^{11}B shifts downfield from Et_2OBF_3; $CDCl_3$ solvent. [b] Broad, unresolved signal. [c] Complex multiplet. [d] Hindered B–N bond rotation (see text). [e] Obscured by the Me_2CH signal. [f] J_{HF} values in brackets. [g] J_{CF} values in brackets. [h] Weak signal, not observed.

Table 2. Preparative and Analytical Data for New 1,3,2-Diazaboracyclohexane Derivatives

			anal.[a]	
compound	yield, %	bp, °C/mmHg	% C	% H
3	84	59–60/15	57.33 (57.19)	12.07 (12.00)
4	67	58–64/14	59.33 (60.04)	12.29 (12.24)
5	94	71/0.01	62.24 (62.17)	9.35 (9.12)
6	50	62–65/6.5	49.57 (49.42)	11.51 (11.26)
7	80	55/1.0	54.31 (54.54)	12.04 (11.70)
8	55	100/15	56.41 (56.60)	12.02 (11.87)
9	70	78–80/0.05[b]	59.89 (59.19)	9.67 (9.60)
10	78	83–85/2.0	49.69 (49.57)	11.12 (11.23)
11	55	56/0.01	53.23 (53.31)	11.68 (11.56)
12	77	80/0.01	66.20 (65.68)	10.15 (9.92)
13	81	93–100/0.01	62.19 (62.40)	10.48 (10.18)
14	69	88–92/0.05	60.56 (60.49)	9.56 (9.39)
15	77	130–144/0.01	70.31 (70.15)	8.08 (7.98)
16	84	106–109/0.04	57.73 (58.20)	9.77 (9.77)
17	60	120–126/0.02	66.74 (66.14)	8.80 (8.60)
18	82	106–119/0.05[c]	58.24 (57.37)	9.91 (9.91)
21	61	51/0.01	54.04 (53.63)	12.03 (11.70)
22	65	86/0.01	65.81 (65.43)	9.77 (9.80)
23	49	49–51/0.01	55.58 (55.52)	11.69 (11.86)
24	36	88–91/0.02	59.39 (59.02)	5.72 (5.54)
25	39	90–93/0.04	53.70 (53.16)	7.56 (7.61)
26	37	110–120/0.01	59.61 (60.03)	7.26 (7.23)
27	*d*	*e*	63.26 (63.59)	7.71 (7.88)

[a] Calculated values in parentheses. [b] Mp 60–62 °C. [c] Mp 85–87 °C. [d] Quantitative yield indicated by NMR spectroscopy. [e] Decomposition during distillation; elemental analysis obtained on undistilled product.

under vacuum. The following procedures are typical of those used for the preparation of the new compounds in this study.

Preparation of *N*-Trimethylsilyl Derivatives. Compounds 5 and 6. A solution of the *N*-lithio derivative of the 1,3,2-diazaboracyclohexane **1** was prepared by the slow addition of *n*-BuLi (41 mL, 101 mmol, 2.5 M hexane solution) to a stirred solution of **1** in THF (150 mL) at 0 °C. The mixture, which became cloudy, was stirred at 0 °C for 2–4 h. Chlorotrimethylsilane (13 mL, 102 mmol) was added via syringe, and the mixture was stirred overnight at room temperature. Following filtration and solvent removal, compound **5** was isolated by fractional distillation as a colorless liquid. The B–Me analog **6** was prepared from **2** by means of the same procedure.

Compounds 7 and 8. A 250-mL, one-necked flask was equipped with **3** (4.4 g, 35 mmol), hexane (100 mL), and TMEDA (5.3 mL, 35 mmol). At room temperature, *n*-BuLi (14 mL, 35 mmol, 2.5 M hexane solution) was slowly added via syringe. The cloudy white suspension was refluxed for 1 h to ensure complete anion formation. After the mixture was cooled to room temperature, Me_3SiCl (4.4 mL, 35 mmol) was added and the resultant mixture was stirred overnight. Following filtration and solvent removal, fractional distillation afforded **7** as a colorless liquid. Compound **8** was prepared form **4** by means of the same procedure.

Compounds 9 and 10. The *N*-lithio derivative of the monosilylated ring **5** (or **6**) was prepared in THF solution at 0 °C as described above in the synthesis of compound **5**. Addition of Me_3SiCl and a similar workup procedure gave **9** (or **10**) as a colorless liquid.

Compound 11. *n*-Butyllithium (7.3 mL, 18 mmol, 2.5 M hexane solution) was added to a solution of **7** (3.6 g, 18 mmol) in hexane (80 mL) and TMEDA (2.7 mL, 18 mmol). The colorless solution turned bright yellow, but there was no evidence of the white precipitate that normally indicated anion formation in the other systems. The mixture was refluxed for 2 h and then stirred overnight. Chlorotrimethylsilane (2.3 mL, 18 mmol) was added, and the solution was stirred overnight. Filtration, solvent removal, and distillation gave **11** as a colorless liquid.

Preparation of *t*-BuMe$_2$Si Derivatives. Compound 12. A 500-mL, three-necked flask, equipped with a reflux condenser, stir bar, and a gas inlet, was charged with **1** (24.4 g, 153 mmol), TMEDA (23 mL, 154 mmol), and hexane (ca. 200 mL). Upon cooling of the mixture to 0 °C, *n*-BuLi (62 mL, 154 mmol, 2.5 M in hexane) was slowly added via syringe and the solution was stirred for 2 h at room temperature. Also at room temperature, *t*-$BuMe_2SiCl$ (23.2 g, 154 mmol) was added. Since there was no visible change, the solution was refluxed for 5 days. After filtration and solvent removal, a viscous opaque yellow liquid remained. Distillation afforded **12** as a colorless liquid.

Compound 13. A 250-mL, three-necked flask, equipped with a reflux condenser, gas inlet, and septum, was charged with **5** (14.6 g, 53 mmol), TMEDA (8.8 mL, 59 mmol), and hexane (100 mL). At room temperature, a quantity of *n*-BuLi (23.4 mL, 59 mmol, 2.5 M hexane solution) was slowly added. Approximately halfway through the addition, the solid anion derivative appeared and the solution became warm. This anion suspension was stirred for 1 h at room temperature and was then refluxed for 1 h to ensure complete lithiation. After cooling of the mixture to room temperature, Me_3SiCl (7.4 mL, 59 mmol) was slowly added, and the solution immediately turned clear and became warm. A small amount of precipitate formed and adhered to the walls of the reaction vessel. After 2 days of stirring, the solvent was removed under vacuum to leave a dark orange clear liquid. Distillation afforded **13** as a bright yellow liquid.

Preparation of *N*-Boryl Derivatives of the Ph–B Ring (Compounds 14–18). The *N*-lithio derivative of the parent B–Ph ring **1** (or its monosilyl derivative **5**) was prepared in THF solution as described above in the synthesis of compounds **5** and **6**. The appropriate chloroborane, $Me_2NB(R)Cl$ (R = Ph, NMe_2), was added at 0 °C via syringe, and the mixture was stirred overnight. After filtration and solvent removal, the *N*-boryl derivatives **14–17** were isolated by fractional distillation as colorless liquids. The bis(boryl) derivative **18** was prepared by the same procedure from the monosubstituted ring **14**.

Preparation of the Chloroboryl Derivatives 19 and 20. Phenyldichloroborane (1.5 g, 9.2 mmol) was added to a stirred solution of **9** (2.8 g, 9.2 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 2 h. Solvent removal left **20** as a gummy solid that was identified by NMR spectroscopy (Table 1). Compound **20**, however, could not be distilled or otherwise purified without extensive decomposition to unidentified products. A similar reaction of **5** with $PhBCl_2$ gave **19** in solution, but this product decomposed upon solvent removal. Addition of 1 equiv of Me_3SiNMe_2 to either **19** or **20** in CH_2Cl_2 solution resulted in its smooth conversion to the B–NMe_2 derivative **15** or **17**, respectively.

Preparation of *N*-Boryl Derivatives of the *i*-Pr and *t*-Bu Ring Systems (Compounds 21–23). A 250-mL, one-necked flask was charged with **3** (4.4 g, 35 mmol), hexane (100 mL), and TMEDA (5.3 mL, 35 mmol). At room temperature, *n*-BuLi (14 mL, 35 mmol, 2.5 M hexane solution) was slowly added via syringe. The cloudy white suspension was refluxed for 1 h to ensure complete anion formation. After the mixture was cooled to room temperature, $(Me_2N)_2BCl$ (4.7 g, 35 mmol) was added, and the resultant mixture was stirred overnight. Following filtration and solvent removal, fractional distillation afforded **21** as a colorless liquid. Compound **3** was converted to **22** [using $Me_2NB(Ph)Cl$], and the *t*-Bu analog **4** was converted to **23** [using $(Me_2N)_2BCl$] by means of the same procedure.

Preparation of the CF_3CH_2O–B Derivative 24 by Si–N Cleavage. A 100-mL, three-necked flask, equipped with a stir bar, gas inlet, and septum, was charged with **7** (3.9 g, 20 mmol) and freshly distilled CH_2Cl_2 (ca. 30 mL). At room temperature, $CF_3CH_2OB(Ph)Cl$ (4.4 g, 20 mmol) was added slowly. The solution, which immediately turned cloudy, was stirred overnight. After solvent removal, the reaction mixture was filtered through a fine filter frit to remove some dark orange suspended matter, leaving a clear orange liquid. Distillation through a short-path apparatus afforded **24** as a colorless liquid.

Preparation of the CF_3CH_2O–B Derivatives 25 and 26 by Dehydrohalogenation. A 250-mL, three-necked flask, equipped with a stir bar,

gas inlet, and septum, was charged with **7** (4.0 g, 20 mmol), Et_3N (3.5 mL, 25 mmol), and hexane (ca. 50 mL). The solution was cooled to 0 °C, and $CF_3CH_2OB(Ph)Cl$ (4.4 g, 20 mmol) was added dropwise. A white precipitate immediately appeared, and the mixture was warmed to room temperature and stirred overnight. After filtration and solvent removal, distillation afforded **25** as a colorless liquid. Compound **26** was similarly prepared from the *N*-*t*-BMe_2Si-substituted ring **12** and $CF_3CH_2OB(Ph)Cl$.

Preparation of the Cl–B Derivative 27 by Si–N Cleavage. The unsymmetrical disilyl ring system **13** (6.9 g, 20 mmol) was dissolved in freshly distilled CH_2Cl_2 (80 mL), and the solution was cooled to 0 °C. Phenyldichloroborane (3.2 g, 20 mmol) was slowly added, upon which the solution turned light yellow. After 1 h of stirring at room temperature, the ^1H NMR spectrum showed the presence of the starting material **13** and the target compound **27**. After overnight stirring, the NMR spectrum of the solution showed only compound **27**. The solvent was removed, leaving an orange gum which gave NMR spectral data consistent with structure **27** and a satisfactory elemental analysis. An attempt was made to distill compound **27**, but the crude residue turned into a translucent brown glass and no distillate was obtained.

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