Reactions of Group 13 and 14 Hydrides and Group 1, 2, 13 and 14 Organyl Compounds with (*tert*-Butylimino)(2,2,6,6-tetramethylpiperidino)borane

Ulrike Braun,[a] Barbara Böck,[a] Heinrich Nöth,*[a] Ingo Schwab,[a] Manfred Schwartz,[a] Siegfried Weber,[a] and Ulrich Wietelmann[a]

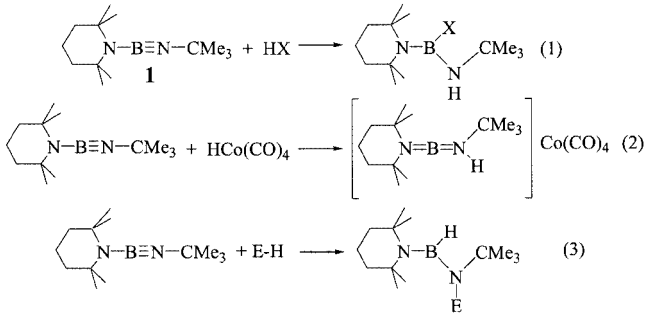
Dedicated to Professor Dr. Dr. h. c. mult. Ernst Otto Fischer on the occasion of his 85th birthday

Keywords: BN triple bonds / Insertion reactions / (*N*-Metal-*tert*-butylamino)(2,2,6,6-tetramethylpiperidino)boranes / Multinuclear NMR / X-ray structures

(*tert*-Butylimino)(2,2,6,6-tetramethylpiperidino)borane (**1**) is a highly reactive species. Its B≡N triple bond inserts into the B–H bond of boranes, R_2BH, generating diborylamines of the type tmp–BH–N*t*Bu–BR_2 (tmp = 2,2,6,6-tetramethylpiperidino; R = H, Cl, Br, or organyl). Thexylborane reacts analogously, but only one of its two B–H bonds is used for the hydroboration of **1**. However, dihaloboranes $HB(Hal)_2$–SMe_2 (Hal = Cl, Br) give *B*-haloboration products tmp–B(Hal)–N*t*Bu–BH(Hal), while reactions with $H_2B(Hal)$–SMe_2 produce a mixture of two isomers by competing hydroboration and haloboration reactions. Tmp–BH–N*t*Bu–AlH_2 was obtained from **1** and AlH_3–NMe_3. It is a dimer in the solid state with pentacoordinate Al atoms and AlH_2Al bridges. Hydrosilylation of **1** was achieved with Me_2SiHCl, $SiHCl_3$ or Ph_2SiH_2 to give the *N*-silyl-substituted diaminoboranes tmp-BH-N*t*Bu–$SiX_{3-n}R_n$. Me_3SnH and Bu_3SnH behave similarly, giving the corresponding *N*-stannylated diaminoboranes. However, when Ph_3SnH was treated with **1**, the stannylborane tmp–B($SnPh_3$)–NH*t*Bu was formed showing an umpolung of the hydrostannylation. Organyllithium compounds provide access to *N*-lithiodiaminoboranes of the type tmp–BR–N*t*Bu–Li. The stability of these compounds depends on the substituent R. The least stable compound was the B–*t*Bu derivative followed by the *B*-methyl compound. However, in the presence of TMEDA tmp–BMe–N*t*Bu–Li is sufficiently stable to allow reactions, e.g. with *B*-chlorocatecholborane, to produce tmp–BMe–N*t*Bu–$BO_2C_6H_4$. The most stable lithium compound so far is tmp–BPh–N*t*Bu–Li–OEt_2, whose structure has been determined by X-ray crystallography. $MgBu_2$ behaves like LiR and both of its Mg–C bonds can be used for the insertion reaction. The same is also true of $ZnMe_2$. In contrast, at ambient temperature, only one of the E–C bonds of triorganylalanes, triorganylgallanes and $InPh_3$ is used for the insertion reaction. In the solid state, most of the new compounds show a weak to strong coordinate bond between the electrophilic centre (Li, Mg, Zn, Cd, B, Al, Ga and In) and the nitrogen atom of the tmp group which generates a four-membered ring.

Introduction

Iminoboranes, RN=BR′, featuring a B≡N triple bond are highly reactive chemical species due to their unsaturated character. Their reactivity exceeds that of the corresponding isolobal alkynes, a consequence of the higher polarity of the B≡N bond compared with the less polar C≡C bond of alkynes. The chemistry of iminoboranes has been reviewed in two comprehensive articles.[1,2] Iminoboranes have a high tendency to dimerize to 1,3-diaza-2,3-diboretidines or trimerize to borazine derivatives.[3,4] In the case of the (*tert*-butylimino)(2,2,6,6-tetramethylpiperidino)borane (tmp−B=N−*t*Bu, **1**) the rate of dimerization is retarded for steric and electronic reasons.[4] Besides this and related cycloaddition reactions, the (amino)(imino)boranes add to carbonylmetal fragments at the imino nitrogen atom of **1**. They also add protic acids HX or an E−X bond of sufficiently strong Lewis acids EX_n across the B≡N triple bond.[1,2] Here we



[a] Department of Chemistry, University of Munich, Butenandtstr. 5−13, 81377 Munich, Germany
E-mail: H.Noeth@lrz.uni-muenchen.de

  DOI: 10.1002/ejic.200300820

report a systematic study of the behaviour of **1** towards hydrides of group 13 and 14 as well as organyl derivatives of the group 1, 2, 13 and 14 elements. Several hydroboration reactions of iminoboranes are already known,[1,2,5] but these and (amino)(imino)boranes offer even more interesting scopes.[6,7]

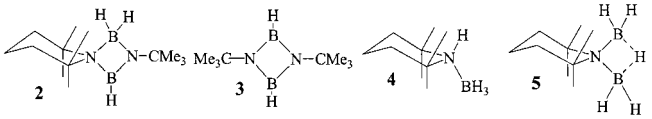
Usually, acidic polar hydrogen compounds HX [X = halogen, OR, SR, NHR, NR_2, $Co(CO)_4$] react with **1** by protonation of the *tert*-butylimino nitrogen atom according to Equation (1). In the case of bulky X groups, for instance $Co(CO)_4$,[8] diaminoborinium salts are formed as shown in Equation (2). This indicates that the first step in reaction (1) is the protonation of the imino nitrogen atom. On the other hand, when hydrides of electropositive elements, $ER_{rn-n}H_n$, are allowed to react with **1**, then the hydrogen atom of an E−H bond attacks at the boron atom.[2] This finally results in the formation of *N*-substituted diaminoboranes tmp−BH−N*t*Bu−$ER_{m-n}H_{n-1}$ as shown in Equation (3). Reaction (3) starts with an electrophilic attack at the N atom of the $NCMe_3$ group by the Lewis acidic centre of the element hydride $ER_{m-n}H_n$, followed by a hydride transfer to the boron atom. This kind of reaction will not occur if the central E atom is too weak a Lewis acid.

In this work we report on the behaviour of various hydrides of boron, aluminium, silicon and tin as well as of organyl compounds of lithium, magnesium, zinc, cadmium, boron, aluminium, gallium and indium.

Results

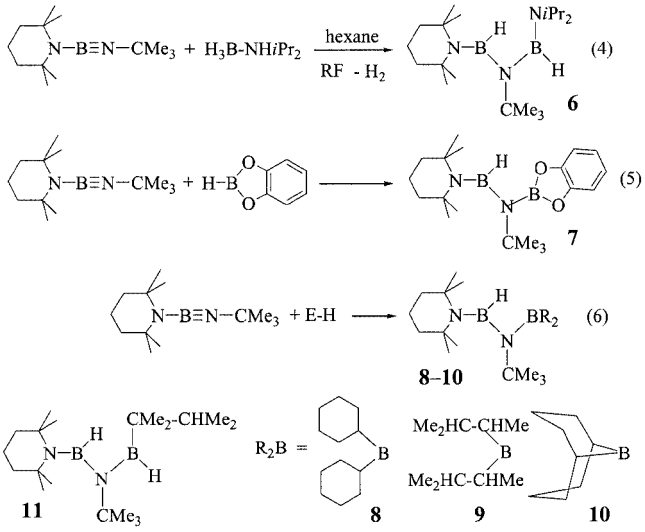
Reactions with Hydrides of Boron and Aluminium

We have already recently reported on the reaction of BH_3−THF with **1**.[5] When diborane is used as the source of BH_3 in the presence of hexane as a solvent, four compounds, **2**−**5**, besides the dimer of **1**, can be detected. After warming the reaction mixture from −196 °C to ambient temperature, ^{11}B NMR signals were found at δ = 28.7 and −4.4 (for **2**), 37.2 (for **3**), −20.8 (for **4**), and −26.2 ppm (for **5**). However, when BH_3−THF was used, the product distribution depended both on the concentration and the temperature of the solutions. At −60 °C, dilute solutions favoured the formation of **2**. Yields up to 82% can be achieved.



An almost quantitative conversion of **1** to **2** can be achieved, however, by employing H_3B−SMe_2 as the hydroborating reagent. In this case, it is important to add a hexane solution of **1** slowly at ambient temperature to a solution of H_3B−SMe_2 in hexane. Under these conditions the dimerization of **1** is prevented due to the presence of a local excess of the borane reagent.

On the other hand, no hydroboration of **1** was observed when employing the aminoboranes H_3B−NEt_3 or H_3B−$NHiPr_2$ at ambient temperature. However, when a solution of **1** and H_3B−$NHiPr_2$ was kept at reflux in hexane, hydrogen gas was formed besides the diborylamine **6** as shown in Equation (4). Hydroboration of **1** can also be achieved with catecholborane, dicyclohexylborane, diisoamylborane or 9-borabicyclo[3.3.1]nonane (9-BBN) as shown in Equations (5) and (6).



Because the B≡N triple bond of **1** also inserts into the B−C bond of triorganylboranes (vide infra), there might be competition between the insertion of the B−C bond and the B−H bond if both are present in the molecule. The results with the diorganylboranes indicate convincingly that the B−H bond is more reactive than the B−C bond, although thermodynamically there should be no strong difference between the two since the number of B−C and B−H bonds does not change. Kinetic investigations into the hydroboration of alkynes have shown that the rate of hydroboration depends on the equilibrium between the dimeric borane and the monomeric borane.[9,10] In spite of the high steric requirements of the diorganylboranes used in this study, all three compounds reacted chemoselectively. However, the rates of the reactions were quite different. 9-BBN reacted fastest and the reaction was complete within 2 h. Disiamylborane required 24 h and dicyclohexylborane needed 96 h. Amongst these, the dicylohexylborane is certainly the least bulky. Nevertheless, it showed the lowest rate. This is because the concentration of its monomeric unit is very low compared with those of the other species.[9] One factor that governs the monomer/dimer equilibrium is the strength of the BHB bridge bond as demonstrated by the corresponding BHB bridge frequencies in the IR spectra. These frequencies are 1590 cm^{-1} for dicyclohexylborane,[11] 1551 cm^{-1} for disiamylborane[12] and 1560 cm^{-1} for 9-BBN.[13] In contrast to these diorganylboranes, the symmetric dithexyldiborane shows a BHB band at 1565 cm^{-1} which is very close to that of the dimeric disiamylborane.[14] However, 8 d are required for a quantitative conversion of

1 into **11**. In contrast to the hydroboration of organic substrates with thexylborane,[14–16] only one of its two B–H hydrogen atoms is used for the hydroboration of **1**.

In contrast, the haloboranes $H_{3-n}B(Hal)_n$ in the form of their Me_2S adducts react with **1** by hydroboration and/or haloboration. The dihaloboranes $HBCl_2$ and $HBBr_2$ show high positive charges at the boron atoms, e.g. +0.976 in $HBCl_2$ (see Table 1) which is almost the same as for BCl_3 but less than in BH_2Cl. Bond dissociation energies may also play a role and should favour the hydroboration route.[17] Both $HBCl_2$–SMe_2 and $HBBr_2$–SMe_2 exclusively give, however, the haloboration products **12** and **13** [Equation (7)]**.** This can be readily demonstrated by the absence of a doublet in the ^{11}B NMR spectrum for the tricoordinate B atom but the presence of a doublet for the tetracoordinate boron atom. This also confirms that compounds **12** and **13** have cyclic structures.

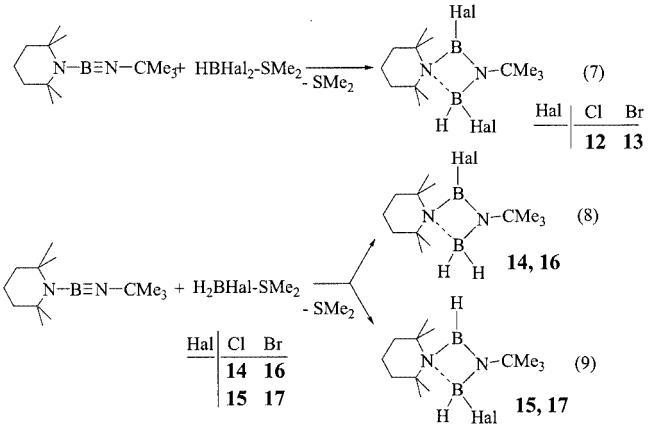


Table 1. Calculated charge densities for the series of chloroboranes $BH_{3-n}Cl_n$

	BH_3	H_2BCl	$HBCl_2$	BCl_3
q_B	0.495	0.724	0.976	0.9995
q_H	−0.165	−0.209	−0.149	
q_{Cl}	–	−0.307	−0.414	−0.3332

On the other hand, reactions of H_2BCl–SMe_2 and H_2BBr–SMe_2 with **1** lead to a mixture of the hydroboration products **15** and **17** with the haloboration products **14** and **16**. The product ratio of **14/15** was 33:66 while it was 50:50 for **16/17**. Therefore, there is a statistical preference for the hydroboration product **15** but not for **17**.

In order to obtain an insight into the formation of compounds **14** and **15**, we performed calculations at the B3LYP/6-311g and B3LYP/8-311+g(2d,f) levels for the model system $ClBH_2/H_2N–B=N–Me$. The results are summarised in Table 2 and shown in Figure 1. The two B–N bonds of the (amino)(imino)borane are in agreement with a higher bond order for the imino nitrogen atom, but also the B–N bond of the amino group NH_2 reveals π-bonding. Thus, the electronic structure of $H_2N–B=N–Me$ is best described by the two formulae **A** and **B**.

$$\underset{\mathbf{A}}{H_2N–B{\equiv}N–Me} \leftrightarrow \underset{\mathbf{B}}{H_2N{=}B{=}N–Me}$$

The adduct **C**, which is considered to be the first step in the hydro/haloboration of $H_2N–B=N–Me$, is more stable by 110.68 kJ/mol compared with the reagents. The adduct shows an allene-type configuration with a torsion angle H–N–N–C of −95.7°. The B–N bond lengths for the $H_2N–B$ and $B–NMe(BH_2Cl)$ groups were calculated as 1.357 and 1.309 Å while the B–N bond to the monochloroborane unit is 1.606 Å. This type of structure has been deduced from NMR spectroscopic data for **1**–ECl_3 (E = Al, Ga)[18] or **1**–$M(CO)_5$ (M = Cr, W)[19] and determined by X-ray crystallography for tmp=B=N*t*Bu(ECl_3) [E = Ga, and In with 1.345(2) and 1.316(2) Å, respectively].[20] These data are in agreement with B=N double bonding between the dicoordinate B atom and the tricoordinate N atoms (see Figure 1).

The adduct **C** is, however, less stable than the chloroboration/hydroboration compounds **D** and **E**. The hydroboration product **E** is more stable by 154.46 kJ/mol than **C**, while the chloroboration product **D** is more stable by178.76 kJ/mol. As expected, the energy difference between **D** and **E** of 24.21 kJ/mol is not large. In each case, the "open chain" structures are energetically favoured over the ring structures **F** and **G**. The energy difference between **D** and **F** is 65.47 kJ/mol in favour of **D**, while **E** is 65.62 kJ/mol more stable than the ring compound **G**. Thus, chloroboration to **D** is the thermodynamically more favourable reaction. This is in contrast to the observed preferred hydroboration of **1** with BH_2Cl. Thus, the model system does not mirror the experimental system.

The calculated B–N bond lengths in **E** are in agreement with B=N double bonding. The shortest B–N bond (1.395 Å) was calculated for an $H_2N–B$ bond while those to the BH_2 group are longest at 1.417 Å. However, the "central" B–N bond is also short at 1.449 Å. This indicates a bonding situation also found in 1,3-butadienes. In the case of **D** and **E**, the *cis* conformations were found to be energy minima. As can be seen from the B–N bond lengths of the ring structure **F** (see Table 2), there is only one N bond with double bond character. The $H_2N\cdots BH_2$ bond is rather long at 1.701 Å and the N and B atoms now exhibit tetracoordination. Although compound **F** shows three B–N single bonds and one B–N π-bond, one B–N bond in particular is quite weak and this is certainly the reason why the chain compound **D** with three B–N π-bonds is more stable. On the other hand, although the chloroboration chain compound **D** is favoured over the hydroboration product **E**, the ring isomer **G** is definitely more stable than the ring **F**. One of the reasons for this is that the B–N bond of the group $H_2N–BHCl$ is much shorter than in **F** which leads to its stabilisation. However, as shown experimentally for compound **14** and **15**, only the ring structures were experimentally observed and not the open-chain compounds as the

Table 2. Model compounds optimised at the B3LYP level of theory; all structures are without imaginary frequencies, i.e. they are real minima; relative energies refer to $E(BH_2Cl)$ + E(iminoborane) = 0. 1 Hartree = 627.5095 kcal/mol = 2627.2568 kJ/mol

	B3LYP/6-311g				B3LYP/b3lyp/6-311+g(2df,p)			
	$-E$ [a.u.]	$-E$ [kJ/mol]	*zpe* [kJ/mol]	B−N [Å]	$-E$ [a.u.]	$-E$ [kJ/mol]	*zpe* [kJ/mol]	B−N [Å]
BH_2Cl	−486.28		55.36	−	−486.31	0	55.37	
Iminoborane	−175.51		19.00	1.24723	−175.57	0	18.56	
				1.39743				
Adduct1		−110.6829	26.10	1.30918		−89.1037	25.64	
				1.35696				
				1.60588				
Adduct2		−265.1378	26.50	1.39564		−253.5101	26.23	
				1.41705				
				1.44942				
iso-Adduct2		−289.3429	26.70	1.39874		−275.8459	26.24	
				1.40058				
				1.46438				
Ring		−199.6628	26.70	1.35622		−192.7342	26.49	1.67613
				1.53900				
				1.57649				
				1.70103				
iso-Ring		−223.7185	26.76	1.37194		−204.2356	26.52	1.64624
				1.53374				
				1.57333				
				1.65177				

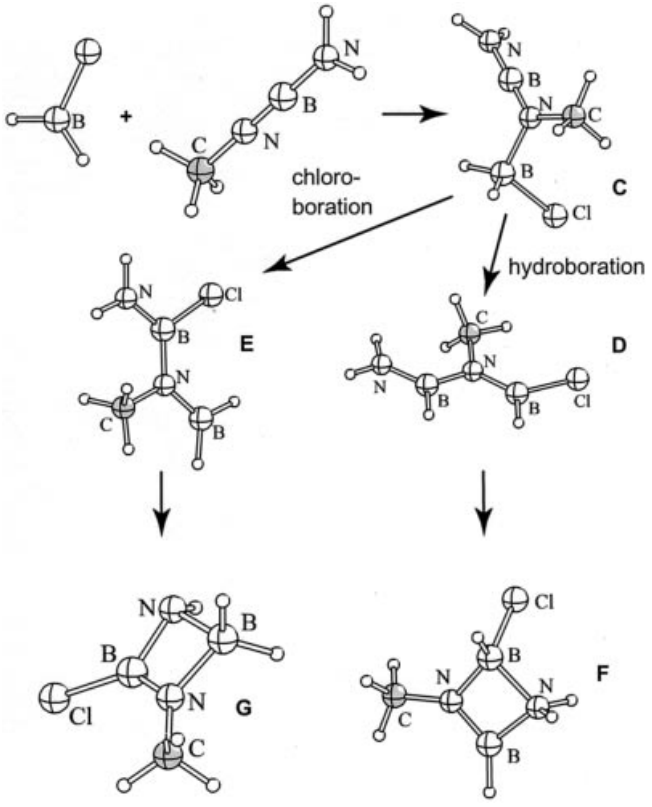


Figure 1. Optimised structures in the $BH_2Cl/H_2N-B=N-Me$ system

calculations suggest and this may be due to the fact that the amino nitrogen atom of the tmp unit is more basic than the NH_2 group of the model system.

For this reason we also performed calculations on tmp−BPh−N*t*Bu−BH_2 whose ring structure was determined by X-ray crystallography.[21] Indeed, optimization of the open-chain structure leads to the ring as the most stable species (Figure 2). The calculated B−N bond lengths compare favourably with the experimental values [experimental: PhB−N 1.594(3), PhB−N*t*Bu 1.367(3), *t*BuN−BH_2 1.555(3), H_2B−N(tmp) 1.665(3) Å, calcd. 1.618, 1.377, 1.561, 1.691 Å]. Clearly, a sufficiently basic N atom of the amino group is needed to favour the ring structure over the open-chain isomer.

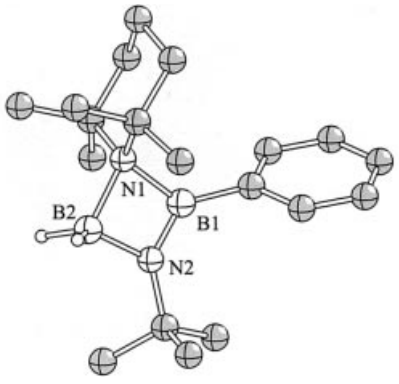
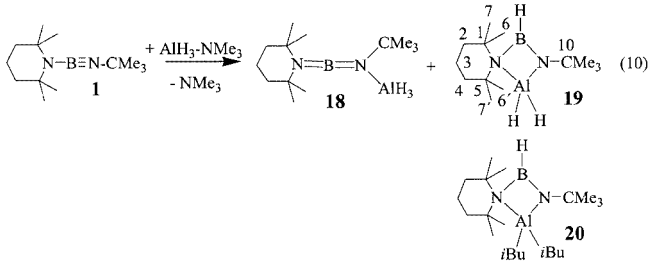


Figure 2. Optimised structure for tmp−BPh−N*t*Bu−BH_2 at the B3LYP/6-311G level of theory

Compound **1** forms adducts of type **C** with $AlCl_3$, $AlBr_3$, $GaCl_3$ and $InCl_3$[18,20] and no insertion reactions have so far been observed for these trihalide adducts in contrast with halosilanes.[22] It was, therefore, of interest to study the

behaviour of AlH_3. This hydride was employed as AlH_3-NMe_3 [see Equation (10)].



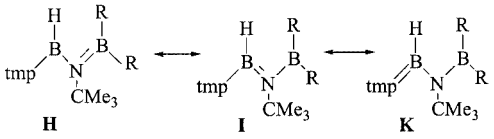
The reaction was followed in hexane solution by ^{11}B NMR spectroscopy which showed that two products were formed. Two new ^{11}B NMR signals appeared at $\delta = 33$ and 27 ppm in a ratio of 1:4. In the proton coupled ^{11}B NMR spectrum, the signal at $\delta = 27$ ppm was a doublet showing that this boron atom carries one hydrogen atom as expected for a hydroalumination product. Two ^{27}Al NMR signals at $\delta = 115$ and 80 ppm in an intensity ratio of 1:4 support the formation of two products. While the low-field signal points to the presence of a tetracoordinate Al atom, the other represents a pentacoordinate Al centre. The intensities of the ^{11}B and ^{27}Al signals change with time. The two high-field signals gain intensity and the low-field signals decrease correspondingly. Moreover, the IR spectrum contains a strong band at 1806 cm^{-1} which is typical for an antisymmetric NBN vibration. These latter data are in agreement with the formation of compound **18**.

Attempts to separate the two compounds by fractional crystallisation from toluene were unsuccessful. The solid obtained showed the same NMR signals as the original reaction mixture. However, well-formed single crystals of dimeric **19** (vide infra) could be selected from the solid material which separated from a hexane solution.

Diisobutylalane reacted chemoselectively with **1** by hydroalumination to the cyclic compound **20**. No transfer of the organyl group was observed. Thus, this reaction corresponds to the hydroalumination of C−C multiple bonds.[23] Nevertheless, compound **20** could not be obtained in a pure form. The reaction of $[(t\text{BuO})_2\text{AlH}]_2$ [24] produced a mixture of three compounds according to the ^{11}B NMR spectrum. We were unable to separate these compounds.

NMR and IR Spectra

Table 3 summarises the NMR spectroscopic data of the hydroboration/haloboration products of the (amino)-(imino)borane **1**. For the diborylamines of the type tmp−BH−N*t*Bu−BX_2, one would expect two ^{11}B NMR signals. This is, however, not the case for **8**, **9**, **10** and **11**. Only one broad signal was observed which showed a barely resolved doublet structure, indicating the presence of a BH group. In the proton-decoupled spectra the doublet vanished but the signal was still broad. Chemical shifts which can be compared with those of **8** to **11** occur in (amino)(organyl)boranes $R_2N-B(H)-R$ ($\delta^{11}B = 41-43$ ppm), monomeric aminoboranes R_2N-BH_2 ($\delta^{11}B = 37-39$ ppm) as well as diborylamines of the type $(R_2N)_2B-NMe-BMe_2$ ($\delta^{11}B = 44-46$ ppm) for the Me_2B group.[25] Thus, the observed chemical shifts for **8**−**10**, which show a better shielding than for any of these aminoboranes, indicate not only that B−N π-bonding is present for the BH group but also that there is a weak interaction of the R_2B group with the tmp nitrogen atom. This is in agreement with a bonding description provided by the formulae **H**−**K**.



The contribution of **K** cannot be significant because there are only single ^1H and ^{13}C resonance signals for the methyl groups at positions 6/7 of the tmp unit in compounds **9** and **10** which indicates free rotation about the B−N bond of the tmp group. However, for the disiamylborane **8**, there are two signals for these hydrogen atoms and four ^{13}C resonances. This can be rationalised by the presence of a nonplanar NBNB skeleton or by a slow interconversion between a cyclic and a noncyclic species. In contrast to these diborylamines, those bearing hydrogen and halogen atoms at the boron atoms are of a cyclic nature as evidenced by two ^{11}B NMR signals as well as two ^1H and ^{13}C resonances for the tmp methyl groups. Those of the tricoordinate boron atoms can be found between $\delta = 20.0$ and 28.8 ppm, whereas those of the tetracoordinate boron atoms are in the range of $\delta = 2.8$ to -5.9 ppm. There are six ^1H NMR signals for the NMe_2 groups of tmp in the mixture of the monohalogen derivatives **14**−**17**. One may expect that compounds **14** and **16** should give rise to two signals for the methyl groups of the tmp ligand and four for compounds **15** and **17**. For the cyclic diborylamines one can expect four signals for these methyl groups provided that the ring is not planar. This is the case for the cyclic diborylamine $Cl_2B-Nt\text{Bu}-\text{BCl}-\text{tmp}$.[26] The C-1/5 carbon atoms of the tmp unit in the dichloro derivative **12** are more deshielded than in the monochloro isomers **14** and **15**, an effect of the stronger Lewis acidic character of the Cl_2B group compared with BHCl. Unfortunately, the corresponding ^{13}C NMR spectroscopic data for the bromo compounds are not available. Conversely, the parent cyclic diborylamine **2** shows only two signals for the methyl groups at positions 6 and 7 both in the ^1H and ^{13}C NMR spectra.[5]

Compounds **19** and **20** give two ^1H and ^{13}C NMR signals for the methyl groups of the tmp substituent in agreement with its cyclic structure. However, the proton resonance for **19** is not well resolved and appears as a broad signal. While the ^{11}B NMR signal for **19** at $\delta = 26.8$ ppm is a doublet in the proton-coupled spectrum [$^1J(^{11}B^1H) = 130$ Hz] no Al−H coupling was observed for the broad ^{27}Al signal at $\delta = 80$ ppm ($h_{1/2} = 9670$ Hz) or for that in **18** [$\delta^{27}Al = 32.6$ ($h_{1/2} = 5170$ Hz]. A strong band at 2468 cm^{-1} in the IR spectrum is typical for a terminal ^{11}BH group of a tricoordinate boron atom. Only a broad and unresolved band centred at 1830 cm^{-1} was observed for the AlH_n vibrations.

Table 3. Selected NMR spectroscopic data of compounds tmp−BX−NCMe$_3$−BYY′; chemical shifts in ppm; coupling constants in Hz

	X	Y	Y′	δ^{11}B	δ^1H			δ^{13}C					
					2-H/4 3-H	6/7-H	C*Me*$_3$C-1/5		C-2/4	C-3	C-6/7	C-10	C*Me*$_3$
2	H	H	H	28.8 (d),[a] −4.4 (t)[b]				56.6	37.5	17.2	25.8, 30.1	49.6	30.3
8	H	C_5H_{11}	C_5H_{11}	35.5 (d)[c]	1.59−1.80 (m)	1.47, 1.50	1.44	54.1	36.8	15.7	30.7, 31.2, 34.3, 35.0	574	33.0
9	H	C_6H_{13}	C_6H_{13}	36.1[d]	1.60−1.88 (m)	1.42	1.51	55.9	37.6	15.8	32.9	53.4	34.1
10	H	9-BBN		35.3 (d)[e]	(br. m)	1.38	1.49	55.9	37.2	15.9	32.2	53.6	33.9
11	H	Thex	H	35.9 (d)[f]	(br. m)	1.32	1.36	56.4	37.4	16.2	33.8, 34.6	55.0	33.1
14	Cl	H	H	25.1, −5.9 (t)[g]	0.93−1.28 (m)	1.29, 1.31, 1.51	1.47	55.1	37.7	16.7	30.1, 30.3	54.9	33.6
15	H	Cl	H	30.6 (d),[h] 3.8 (d)[i]	0.93−1.28 (m)	1.32, 1.37, 1.55	1.50	55.1	36.7, 40.6	16.1	30.7, 30.8	51.1	32.9
12	Cl	Cl	H	25.1, 3.5 (d)[k]	0.98−1.41 (m)	1.23, 1.31,	1.37	59.8, 60.2	37.1	16.6	25.3, 26.7 30.5, 31.7	51.6	30.7
16	Br	H	H	30.8, 2.4 (t)[k] [l]	0.98−1.41 (m)	1.24, 1.26	1.59		38.7				
17	H	Br	H	32.3,[m] 1.0 (d)[n]	0.8−1.15 (m)	1.28, 1.29 1.35, 1.36	1.40						
13	Br	Br	H	22.6, 0.8 (d)[q]	0.8−1.15 (m)	1.20, 1.24, 1.63, 1.78	1.40						

[a] $^1J(^1H^{11}B)$ = 1.56. [b] $^1J(^1H^{11}B)$ = 111. [c] $^1J(^1H^{11}B)$ = 112. [d] $^1J(^1H^{11}B)$ = 119. [e] $^1J(^1H^{11}B)$ = 82. [f] $^1J(^1H^{11}B)$ = 108. [g] $^1J(^1H^{11}B)$ = 125. [h] $^1J(^1H^{11}B)$ = 142. [i] $^1J(^1H^{11}B)$ = 155. [k] $^1J(^1H^{11}B)$ = 148. [l] $^1J(^1H^{11}B)$ = 75. [m] $^1J(^1H^{11}B)$ = 105. [n] $^1J(^1H^{11}B)$ = 50. [q] $^1J(^1H^{11}B)$ = 105.

Crystal Structure of 19

The cyclic (tmp)borylaminoalane **19** crystallises in the triclinic space group $P\bar{1}$ with $Z = 4$. Therefore, there are two independent monomeric molecules in the unit cell. As shown in Figure 3, the monomers are connected to dimeric molecules via Al−H−Al bridges. The dimeric molecules possess crystallographic inversion centres making each Al atom pentacoordinate. The Al1−N1 bond is 0.242 Å longer than the Al1−N2 bond to the tricoordinate nitrogen atom N2. Also the B1−N1 bond is considerably longer [1.546(5) Å] than the B1−N2 bond [1.369(5) Å] which is typical for B−N π-bonding in monoaminoboranes. The hydrogen bonds between the two Al atoms are asymmetric as shown by the Al(1)−H1 and Al(1A)−H1 bond lengths of 1.65 and 1.46 Å, respectively, while the terminal Al−H bond has a length of 1.48 Å. The four-membered N1−B1−N2−Al1 ring is almost planar, the largest deviation from the mean plane is 0.012(3) Å. The geometry around Al1 is strongly distorted tetragonal-pyramidal. This is of course due to the sharp bond angles N1−Al1−N2 of 72.6(1)° and B1−N1−Al1 of 82.2(1)°. The bond angle N1−Al1−H1 to the apical atoms is 156.7°. As expected, the tmp ring adopts a chair conformation.

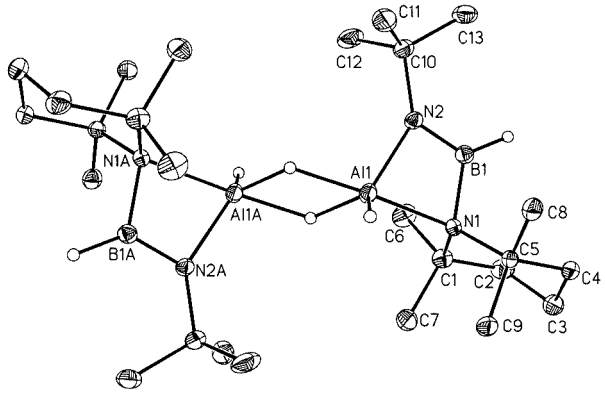
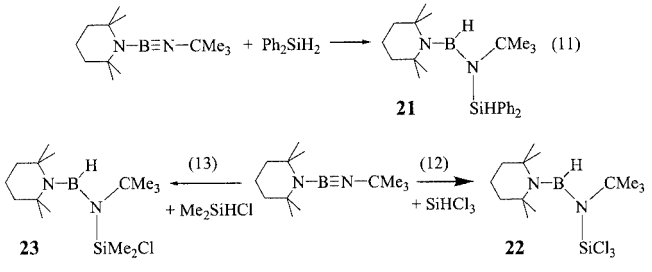


Figure 3. ORTEP representation of the molecular structure of **19**; selected bond lengths [Å]: Al1−N1 2.115(3), Al1−N2 1.873(1), Al1···B1 2.445(4), Al···Al1A 2.813(1), B1−N1 1.546(5), B1−N1 1.369(5), N1−C1 1.534(5), N1−C5 1.582(4), N2−C10 1.483(5), Al1−H1 1.65, Al1−H1A 1.46, Al1−H2 1.48, B1−H1B 1.18; selected bond angles [°]: N1−Al1−N2 72.6(1), N1−B1−N2 108.5(3), Al1−N1−B1 82.2(2), B1−N2−Al1 96.7(2), Al1−N1−C5 116.2(2), Al1−N1−C1 117.2(1), Al1−N2−C10 135.6(2), H1−Al1−H1A 121(1), H1−Al1−H1C 111, Al1−H1−Al1A 130, N1−Al1−H1A 103, N1−Al1−H1 157, H1B−B1−N2 130, H1B−B1−N1 121

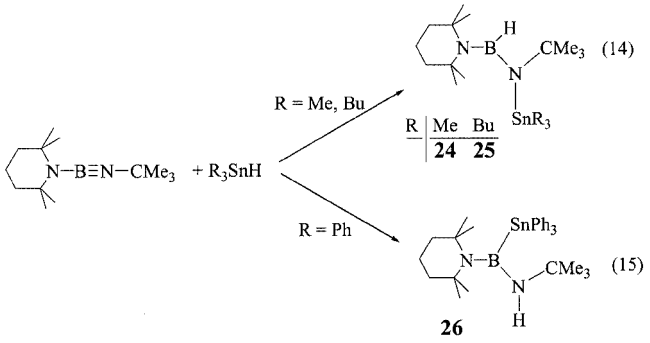
Reactions with Hydrides of Silicon, Germanium and Tin

Within the series of hydrides of the heavier group 14 elements, the bond polarity of the E−H bond changes considerably. Moreover, the hydrides are only weak Lewis acids. Therefore, one may surmise that these hydrides will either not react with **1** or do so only very sluggishly and the hydrogen atom will either move to the boron atom or the nitrogen atom depending on the polarity of the E−H bond. The latter can, of course, be influenced by substituents.

No reaction was observed between Me_3SiH or Ph_3SiH and **1**. However, Ph_2SiH_2 did hydrosilylate **1** according to Equation (11) to yield tmp−BH−N*t*Bu−$SiPh_2H$ (**21**). Moreover, when **1** was treated with Me_2SiHCl or $SiHCl_3$ the corresponding hydrosilylation products **22** and **23** were formed and isolated as viscous oils in good yields.



Me_3GeH and Ph_3GeH did not react with **1** at ambient temperature. At elevated temperature only the dimerization of **1** to its corresponding 1,3,2,4-diazadiboretidine occurred.[4] However, Me_3SnH and Bu_3SnH hydrostannylated **1** as shown in Equation (14) while Ph_3SnH reacted according to Equation (15).



NMR Spectra

In the ^{11}B NMR spectrum of **26** [$\delta^{11}B$ = 44.6 ppm (br., $h_{1/2}$ = 700 Hz)], no $^{11}B^{119}Sn$ coupling could be observed. This is not unusual because of the rapid relaxation due to the quadrupole moment of the ^{11}B nucleus. Also, no ^{119}Sn resonance was found for the same reason. However, a broad ^1H NMR signal at δ = 5.13 ppm indicates the presence of an NH group. Moreover, the IR spectrum of **26** contains a strong band at 3383 cm^{-1} due to the NH vibration.[27] In addition, the ^1H and ^{13}C NMR spectra show three sets of signals for the phenyl groups. Clearly, the vicinity of the bulky tmp substituent induces hindered rotation about the Sn−C bonds. Furthermore, there is only one broad ^1H NMR signal for the methyl group at the tmp substituent and there was no sharpening of the signal at −60 °C. There are, however, two ^{13}C resonances for the methyl groups showing that rotation about the B−N bond is hindered. Most likely, the tmp group stands perpendicular to the N1−B1−Sn1−N2 plane. The final proof of the structure of **26** came from an X-ray diffraction study.

Table 4 shows that the boron nuclei of the two stannylation products of **1** are better shielded than they are in the hydrosilylation products. Moreover, the ^1H and ^{13}C resonances for the tmp methyl groups are at higher field than those of the silyl compounds **21** and **22**. Compounds **21** to **24** all show two ^1H and ^{13}C resonances for these methyl groups indicating hindered rotation. Therefore, one can assume that all these compounds most likely have cyclic structures.

X-ray Structure Analysis of 26

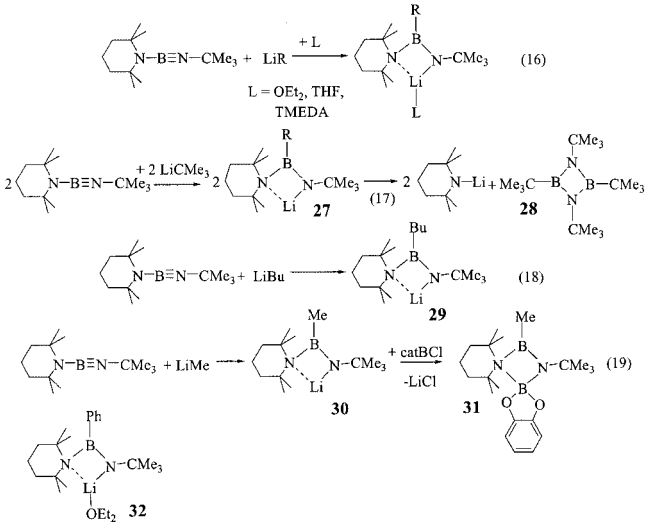
Crystals of **26** are orthorhombic. The space group is $P2_12_12_1$ with Z = 4. Figure 4 depicts the molecular structure of this molecule. It supports the conclusions deduced from the spectroscopic data.

The B−Sn bond length in **26** of 2.295(2) Å corresponds to a single bond as found, for example, in $Me_3Sn(Me_2N)B-B(NMe_2)SnMe_3$ [2.276(2) Å].[28] The two B1−N bonds differ by 0.087(3) Å, the longer bond involves the B−N bond to the tmp group which shows a crown configuration and whose C1−N1−C5 plane includes a twist angle with the N1−B1−N2 plane of 85.2°. The sum of the bond angles at N1 is 354.2° which shows that the N1 atom is almost sp^2-hybridised. There is a strong steric interaction between one of the phenyl groups with the *tert*-butyl group as seen by a B1−N2−C10 bond angle of 137.2(2)°. The torsion angle for the atoms Sn1−B1−N2−C10 is 13.5°, and the tmp substituent (C1−N1−C5) stands almost vertical (91.7°) to the N1−B1−Sn1 plane.

Reactions of Main Group Elements with Organyl Compounds MR_n (n = 1−3)

Reactions with Organyllithium Compounds

Some reactions of organylmetal compounds MR_n with **1** have so far only been described for M = Li and Mg in a review article.[3] In principle, organyllithium compounds should add to **1** according to Equation (16) but the stability of the resultant *N*-lithiodiaminoboranes depends on the nature of R.



For instance, *tert*-butyllithium reacts according to Equation (16) but the product **27** is unstable and decomposes into Li(tmp) and the 1,3,2,4-diazadiboretidine **28** [Equation (17)]**.** In contrast, *n*-butyllithium leads to the stable *N*-lithiodiaminoborane **29**. Methyllithium yields compound **30** which, like **27**, decomposes. However, when the reaction (19) is performed in the presence of tetramethylethylenediamine then **30** can be treated with *B*-chlorocatecholborane to produce the cyclic diborylamine **31**. No reaction occurred between fluorenyllithium and **1**, but phenyllithium reacted smoothly in diethyl ether to give compound **32** which could be isolated as single crystals from a hexane/diethyl ether solution.

X-ray Structural Analyses of 32 and 31

Figure 5 shows the molecular structure of **32**. It features a four-membered LiN_2B ring with a tricoordinate Li atom. The Li1−N2 bond is 0.21 Å shorter than the coordinate Li1−N1 bond. Atom N2 has a planar geometry which al-

Table 4. Selected NMR spectroscopic data of compounds **19**−**25**; chemical shifts δ in ppm; additional data can be found in the Exp. Sect.

	δ^{11}B	δE	δ^{1}H			δ^{13}C					
			2-H/4 3-H	6/7-H	C*Me*$_3$	C-1/5	C-2/4	C-3	C-6/7	C-10	C*Me*$_3$
19	26.8(d)[a]	80[b]	1.49−1.58 m	1.22 1.36	1.06	52.8	38.4	17.1	22.7 31.8	49.3	33.5
20	33.5 (d)[c]	109.5	1.35 1.53	1.23 br.	1.29	55.5	37.4	17.0	26.9, 29.2	50.5	33.8
21	37.7(d)[d]	−21.9	1.5 m, vbr	1.46 br	1.35	54.5	37.2	15.9	33.5 br	54.7	32.9
22	34.6[e]		1.3−1.7 m	1.37 1.40	1.38	55.6	36.7	15.4	32.7 34.8	56.7	31.6
23	35.9[f]		1.2−1.6 m	1.35 1.37	1.38	53.3	37.9	15.4	32.1 35.7	54.9	32.4
24	39.4[g]	−	1.1−1.5 n	1.17 1.28	1.34	52.6	40.4	18.5	26.9 36.1	55.4	34.9
25	39.2	−	1.1−1.5 m	1.18 1.28	1.34	52.6	40.4	18.6	27.3 35.5	55.2	34.0
26	44.6	−	1.40 m br.	1.26	1.13	52.9	39.7	18.7	29.1, 33.4	51.0	32.6

[a] $^{1}J(^{11}B^{1}H)$ = 52. [b] Line width 9670 Hz. [c] $^{1}J(^{11}B^{1}H)$ = 111. [d] $^{1}J(^{11}B^{1}H)$ = 114. [e] $^{1}J(^{11}B^{1}H)$ = 126. [f] $^{1}J(^{11}B^{1}H)$ = 111. [g] $^{1}J(^{11}B^{1}H)$ = 111.

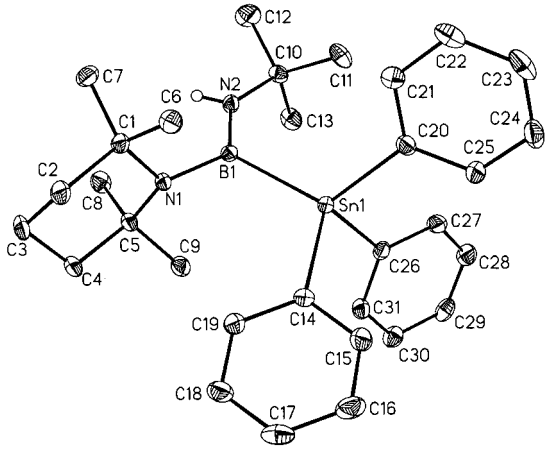


Figure 4. The molecular structure of (*tert*-butylamino)(tetramethylpiperidino)(triphenylstannyl)borane (**26**); selected bond lengths [A]: B1−Sn1 2.295(2), B1−N1 1.476(3), B1−N2 1.389(3), N1−C1 1.496(2), N1−C5 1.492(2), N2−C10 1.485(2), Sn1−C14 2.166(2), Sn1−C20 2.166(2), Sn1−C26 2.166(2); selected bond angles [°]: N1−B1−N2 119.4(2), N1−B1−Sn1 116.4(1), N2−B1Sn1 140.0(2), B1−N1−C1 117.2(1), B1−N1−C5 116.7(1), C1−N1−C5 120.3(2), B1−N2 C10 137.2(2), H2−N2−B1 109(1), H2−N2−C10 112(1), C14−Sn1−C20 104.44(7), C14−Sn1−C26 99.79(7), C20−Sn1−C26 102.74(8)

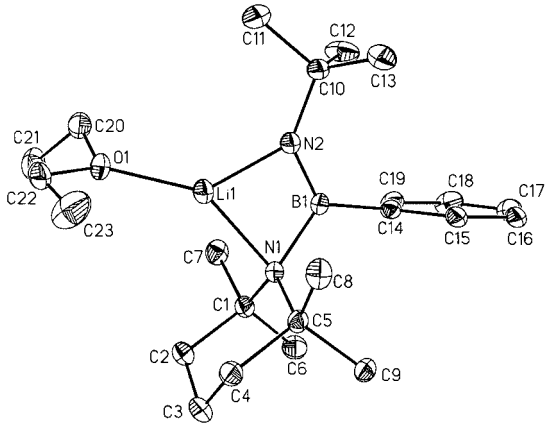


Figure 5. Molecular structure of **32**, ORTEP diagram; selected bond lengths [A]: Li1−N1 2.085(6), Li1−N2 1.884(5), Li1−O1 1.929(5), N1−B1 1.564(4), N2−B1 1.361(4), N2−C10 1.467(4), N1−C1 1.495(4), N1−C5 1.485(4), B1−C14 1.617(4); selected bond angles [°]: N1−Li1−N2 75.70(2), Li1−N1−B1 78.9(2), N1−B1−N2 112.9(2), B1−N2−Li1 91.6(2), N1−B1−C14 126.2(3), N2−B1−C14 120.9(3), N1−Li1−O1 136.2(3), N2−Li1−O1 142.5(3), C1−N1−C5 116.2(2)

lows good B−N π-bonding. The phenyl group stands almost perpendicular to the N1−B1−N2 plane (τ = 89.5°). This prevents B−C π-bonding. The four-membered ring has a flat butterfly structure as shown by an interplanar angle τ = 9.1° for the planes B1−N2−Li1 and B1−N1−Li1. As usual, the tmp ring has a chair conformation. Its N1 atom adopts a distorted tetrahedral geometry with bond angles ranging from 78.9(2) to 118.0(2)°. Although the ring structure of **32** is certain in the solid state, it is very likely that this structure is not retained in solution since only a single signal was observed for the methyl groups at the tmp substituent, both in the ^{1}H and ^{13}C NMR spectra.

An ORTEP plot of the molecular structure of the cyclic diborylamine **31** is shown in Figure 6. It features a planar four-membered B_2N_2 ring. The B1−N1 bond is 0.262 Å longer than the B1−N2 bond [1.378(3) Å]. The B−N bonds to B2 are 1.753(3) Å (N1) and 1.495(3) Å (N2), respectively. The latter is typical for a single bond between an sp^3-hybridised boron atom and an sp^2-hybridised N atom. The long B2−N1 distance corresponds to a weak bond which is in agreement with the NMR spectra which show only one signal for the tmp methyl groups indicating rotation about its B−N bond in solution. Although one might have expected the two B−O bonds to be equal in length, this is not the case and they differ by 0.04 Å. Their lengths are similar to those found for the bis(catecholato)borate anion.[29] The planes N1−C1−C5 and B2−O1−O2 stand almost perpendicular to the B1−N1−B2−N2 ring plane by 92.5 and 89.8°, respectively.

Reactions with Diorganylmagnesium, -zinc, -cadmium and -mercury Compounds

In order to test the possibility of a double insertion of **1** into metal−carbon bonds of dialkylmetal compounds ER_2 (E = Mg, Zn, Cd, Hg), we studied the reaction of **1** with

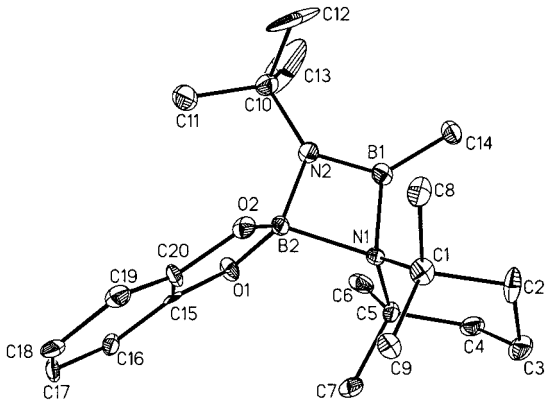
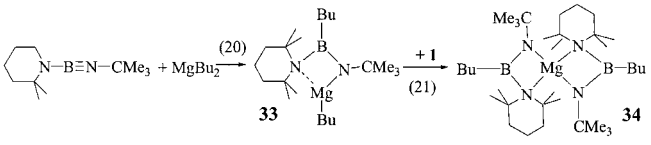


Figure 6. Molecular structure of tmp−BMe−N*t*Bu−Bcat (**31**); selected bond lengths [A]: B1−N1 1.756(4), B1−N2 1.377(4), B1−C14 1.578(5), N1−B2 1.561(4), B2−N2 1.494(4), B2−O1 1.503(6), B2−O2 1.423(6), N1−C1 1.559(6), N1−C5 1.534(6). O1−C15 1.347(5), O2−C20 1.395(5); selected bond angles [°]: B1−N1−B2 79.8(2), N1−B2−N2 86.0(2), B2−N2−B1 95.9(2), N1−B1−N2 98.3(2), B1−N2−C10 134.6(3), B2−N1−C10 129.5(2), C14−B1−N1 129.4(3), C1−N1−C5 114.7(3), O1−B2−O2 105.9(2), O1−B2−N1 112.7(3), O2−B2−N1 115.5(4)

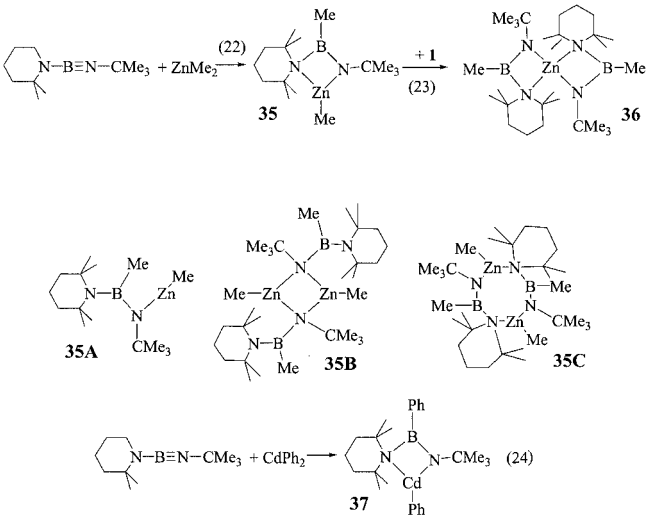
dibutylmagnesium. Reactions (20) and (21) proceeded rapidly at −78 °C. Only a single ^{11}B NMR signal was found at $\delta^{11}B = 37.6$ ppm. This value is typical for metallated diaminoboranes. Compound **33** was obtained as a viscous oil and attempts at crystallisation were unsuccessful. Because the NMR spectroscopic data for **33** and **34** are rather similar to those of the lithium compound **30**, we assume that the magnesium atom is coordinated to the tmp nitrogen atom. Dibutylmagnesium reacts with **1** not only in a 1:1 stoichiometry but also in a 1:2 ratio to produce **34**. This product is also a viscous oil with $\delta^{11}B = 39.0$ ppm.



Dialkylzinc compounds are less reactive than dialkylmagnesium compounds. Nevertheless, **1** reacted with dimethylzinc in toluene to produce a solid 1:1 insertion product **35**, $\delta^{11}B = 39.4$ ppm, as shown in Equation (22). The compound was obtained as single crystals. A reaction in a 1:2 ratio to give **36** was also successful.

As a representative of organylcadmium compounds we studied the reaction of diphenylcadmium with **1** in toluene. Reaction (24) proceeded smoothly to give compound **37**. In contrast, diphenylmercury did not react with **1** either at ambient temperature or in refluxing toluene.

From the solutions of **37**, a few well-shaped crystals separated within several days. These, however, proved not to be compound **37** but rather $CdPh_2$. As far as we know, the structure of this compound has not yet been determined. Therefore, some data for this linear compound are listed in the references.[30] **37** is isostructural with $HgPh_2$.[31]



NMR Spectra

An overview of relevant NMR spectroscopic data of the lithium, magnesium, zinc and cadmium compounds is given in Table 5. The magnesium compound **33** exhibits only single ^1H and ^{13}C NMR signals for the methyl groups at the piperidino ring. This suggests a weak interaction of the Mg atom with the tmp nitrogen atom allowing rotation of the tmp group in solution. A similar situation is, therefore, expected for **34** which shows a broad low-field proton NMR signal for the C-6/7 group but two ^{13}C NMR signals. This can be explained by a hindered rotation about the B−N bond of the $BNCMe_3$ group where the *t*Bu group attached to the boron atom can be oriented either *cis* or *trans* to the *tert*-butyl group. This suggestion is supported by the strong deshielding of the protons of the CMe_3 group in **34**. The ^{11}B NMR signals of the two Mg compounds are rather similar, and the shielding of the boron nuclei are similar to those of the Li and Zn compounds.

The ^1H NMR spectrum of **35** reveals two sharp singlets for the BMe and ZnMe groups in a 1:1 ratio. Also, two ^{13}C NMR signals were observed for these groups. These are sharp for ZnMe ($\delta^{13}C = 11.3$ ppm) and broad for BMe ($\delta^{13}C = 1.0$ ppm). A single resonance represents the methyl groups at tmp and two signals in a 2:1 ratio were found for the CH_2 groups of the piperidino ring. Thus, in solution, the structure of compound **35** may either be monomeric or dimeric. However, in the case of the dimer (**35B**) one would expect a low-field shift of the protons of the CMe_3 group, due to the tetracoordination of the respective nitrogen atom. Because monomeric organylzinc amides are scarce, the alternative **35A** is not very likely. Another possibility might be the dimeric structure **35C** which we regard as unlikely because two sets of NMe_2 group are to be expected. However, the molecular structure of **35** has been shown to be a cyclic *N*-(methylzinc)diaminoborane in the solid state. For this reason we suggest that the structure of **36** is also spirocyclic in solution as found for **35** in the solid state.

Table 5. Selected NMR spectroscopic data of compounds **30** and **32**−**37**; additional data can be found in the Exp. Sect.

	δ^{11}B	δ^{1}H				δ^{13}C					
		2,4-H	3-H	6,7-H	C*Me*$_3$	C-1,5	C-2,4	C-3	C-10	C-11−13	C-6,7
30	39.1	1.41 (t)	1.66 (m)	1.24 (br.)	1.13	51.05	40.83	18.14	8.49	32.26	31.9
32	34.0	1.54 (t)	1.62 (m)	1.30	1.02	52.67	37.89	19.14	49.91	3.86	36.64
33	37.6	0.95	1.68 (m)	1.26	1.18	51.3	39.9	18.0	48.8	32.7	32.3
34	39.0	0.72 (−)	1.59 (br.)	1.23	0.87	53.8	35.7	17.8	52.0	32.0	31.0, 32.5
35	39.5	1.38 (m)	1.66 (m)	1.26	1.13	50.9	40.8	18.1	53.2	32.1	31.8
36	39.1	1.15 (−)	1.64 (br. m)	1.13, 1.24	1.26	51.2	41.0	18.4	53.4	32.1	32.4, 38.6
37	35.4	1.32 (t)	1.54 (m)	1.06, 1.38	1.08	53.2	43.5	17.8	50.6	35.6	25.3, 38.6

The chemical shift $\delta^{11}B = 35.4$ ppm for **37** is compatible with the suggested $PhBN_2$ unit as found in $PhB(NMe_2)_2$ ($\delta = 32.4$ ppm) or $PhB(NEt_2)_2$ ($\delta = 34.1$ ppm).[25] As for **34**, only one ^{1}H NMR signal but two ^{13}C resonances were observed for the methyl groups at tmp in the ^{1}H and ^{13}C NMR spectra. The presence of the Cd atom follows from the satellites observed on the methyl carbon resonance which indicates a $^3J(^{111/113}Cd^{13}C)$ coupling.

Molecular Structure of 35

The zinc compound **35** crystallises in the monoclinic space group $P2_1/c$. Figure 7 shows the ORTEP plot. In the solid state, the methyl[*N*-(methylzinc)-*tert*-butylamino](tetramethylpiperidino)borane is present as a four-membered almost planar ring. Its shape, however, is a strongly distorted trapezoid due to four different endocyclic bond lengths. Endocyclic bond angles range from 70.43(8)° (N1−Zn1−N2) to 98.7(2)° (B1−N2−Zn1). The interplanar angle, τ, between the planes N1−Zn1−N2 and N1−B1−N2 is 2.9°. Notable is the tricoordinate zinc atom (sum of the bond angles = 360°). The B1−N2 bond is quite short at 1.350(4) Å, implying the presence of a B−N π-bond. As in many of the other structures presented here, the B1−N1 bond is long [1.555(3) Å], typical for a single bond. Analogously, the Zn1−N1 bond [2.222(2) Å] is much longer than the Zn1−N2 bond (1.908 Å). The tmp group adopts a chair conformation.

As far as we are aware, the structure of compound **35** is unique since alkylzinc amides $RZnNR_2$ are usually dimeric, containing a four-membered Zn_2N_2 ring.[31,32] The X-ray structure of $(MeZnNPh_2)_2$[33] shows Zn−N bond lengths of 2.080 and 2.066 Å to the tetracoordinate nitrogen atoms. These are much shorter than in compound **35** but longer than the Zn1−N2 bond to the tricoordinate N atom. Dimers of the type $(RZnNR_2)_2$ can be broken up with donors such as pyridine, but no adducts of the type $RZnNR_2(py)$ have yet been characterised in contrast to $RZnNR_2(py)_2$, in which the zinc atom is tetracoordinate.[33]

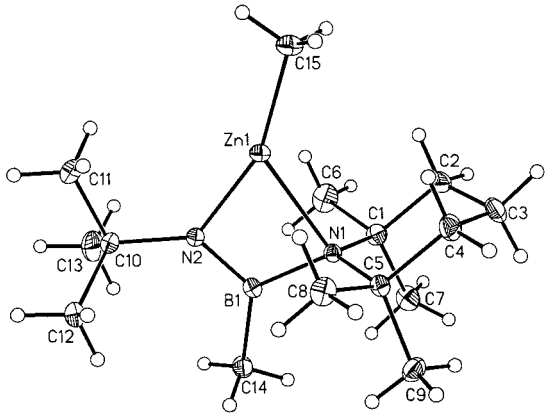
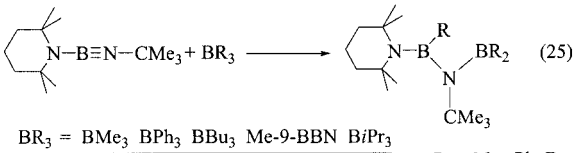


Figure 7. Molecular structure of **35** in the solid state; selected bond lengths [Å]: Zn1−N1 2.222(2), Zn1−N2 1.908(2), Zn1−C15 1.944(3), N1−C1 1.514(3), N1−C5 1.514(3), B1−N1 1.555(3), B1−N2 1.380(4), B1−C14 1.597(4), N2- C10 1.481(3); selected bond angles [°]: Zn1−N1−B1 81.59(2), Zn1−N1−C1 110.9(2), Zn1−N1−C5 110.2(2), N1−B1−N2 109.2(2), N1−B1−C14 122.8(2), N2−Zn1−N1 70.43(8); angles between planes [°]: Zn1N1nB1/Zn1N2B1 2.9, C1N1C5/Zn1N2B1N2 90.0

Reactions with Triorganylboranes, -alanes, -gallanes, and -indanes

The triorganyl compounds of the group 13 elements are medium to strong Lewis acids, the acidity being determined principally by the steric requirements of the organyl group. It was, therefore, expected that no 1:1 adducts would be observed in reactions with **1** because the (amino)(imino)-borane is only a moderate base. Indeed, no evidence for a stable 1:1 coordination compound with triorganylboranes was observed by NMR spectroscopy. However, organoboration of **1** occurs easily, but the rate depends strongly on the steric requirements of the organyl group. This is shown by the data for reaction (25).



BR_3 =	BMe_3	BPh_3	BBu_3	Me-9-BBN	$BiPr_3$
rate (h)	1[a]	16	24	96	336

R = Me, Ph Bu [b] *i*Pr
38 **39** **40** **41** **42**

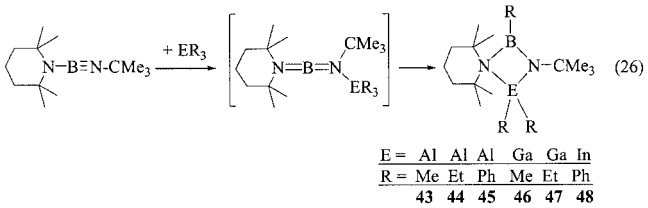
[a] at -78°C

[b] R = Me, BR_2 = 9-BBN

To rationalise these results we assume that there is a pre-equilibrium **1** + BR_3 ⇄ **1**·BR_3. The position of this equilibrium lies more on the side of the individual components the more bulky the R group becomes. Thus, the lower the concentration of the adduct, the slower the reaction rate. In the case of *B*-methyl-9-borabicyclo[3.3.1]nonane, it is the methyl group which moves to the boron atom. Most of

these new asymmetrically substituted diborylamines (**38**−**42**) are liquids.

Although the triorganyl compounds of the heavier group 13 element are all dimeric, they react rapidly with **1** according to Equation (26). Most of the resultant compounds are viscous liquids. Some are solids, however, but single crystals of these could not be obtained.



(26)

E =	Al	Al	Al	Ga	Ga	In
R =	Me	Et	Ph	Me	Et	Ph
	43	**44**	**45**	**46**	**47**	**48**

NMR Spectra

The NMR spectroscopic data of compounds **38**−**41** and **43**−**48** are summarised in Table 6 (ignoring the data for the substituents at element E which are found in the Exp. Sect.). The dialkyl[*N*-(tetramethylpiperidinoboryl)-*tert*-butylamino]boranes **38**−**41** exhibit two ^{11}B NMR signals. In case of **39**, only a single signal was observed. This is not totally surprising since resonances of CBN_2 and C_2BN groups can be close together [Ph_2BNR_2: δ = 40−43 ppm; $PhB(NR)_2$: δ = 33−36 ppm; $(Ph_2B)_2NH$: δ = 41 ppm].[25] In general, for the two groups, those of the C_2BN type are less well shielded than those for CBN_2. In general, boron atoms of diborylamines are less well shielded than boron atoms of aminoboranes. In all cases, two resonances were observed for the C-6/7 atoms revealing hindered rotation about the tmp group. No systematic influence on the δ^{11}B shifts by the group 13 element atoms in compounds **39**−**48** could be observed. Because all show two ^{1}H and ^{13}C signals for the C-6/7 methyl groups, it follows that these compounds most likely have ring structures with E−N1 bonds. This is supported by a ^{27}Al NMR signal at δ = 105 ppm for **43** which is consistent with a tetracoordinate Al atom. On the other hand, the rather broad ^{27}Al NMR signal at δ = 150 ppm for **44** points to a noncyclic structure with hindered rotation about the B−N bond of the tmp group. This conclusion for **43** as well as for **46** is supported by the X-ray structures of tmp−BPh−N*t*Bu−EMe_2 (E = Al, Ga) which will be discussed shortly.[21]

Discussion

The B≡N triple bond of iminoboranes is highly reactive and this has been further demonstrated by results described here for the (amino)(imino)borane **1**. The reaction with diborane is not selective because four different compounds were observed in addition to the hydroboration product **2**. The by-products result from B−N bond cleavages. However, **2** can be formed in high yield by employing $H_3B−SMe_2$ as the borane source. On the other hand, only hydroboration of **1** occurs with diorganylboranes and thexylborane (employed as its dimer). Hence, this reaction is faster than the organoboration of **1** which can be achieved by using triorganoboranes. This can be rationalised by the higher negative charge at the hydrogen atom compared with the organyl group, as well as of the ability of the hydridic hydrogen atom to form hydrogen bonds between two electropositive atoms. The competition between hydroboration and haloboration is chemoselective for the former in the case of the dihaloboranes $HB(Hal)_2−SMe_2$, while in case of monohaloboranes both reactions compete with each other. In this case, the hydroboration should be statistically more favourable. This is indeed observed for $H_2BCl−SMe_2$ but not for $H_2BBr−SMe_2$. In the latter case the observed 1:1 product ratio of the two isomers shows that bromoboration is favoured. If the determining factor were the partial negative charges at the hydrogen and halogen atoms, then the haloboration should win the competition as observed for $HB(Hal)_2$. From this point of view it was most surprising to find that $HSiCl_3$ reacts with **1** exclusively by hydrosilylation, although statistically the chlorosilylation of **1** should be favoured and this is indeed observed when em-

Table 6. Selected NMR spectroscopic data of compounds **38**−**48**; chemical shifts δ in ppm; additional data can be found in the Exp. Sect.

	δ^{11}B	δ^{11}B/^{27}Al	δ^{1}H				δ^{13}C					
			2,4-H	3-H	C*Me*$_2$	C*Me*$_3$	C-1/5	C-2/4	C-3	C-6/7	C-10	C-11−13
38	40.7	45.7	1.53 (br.)		1.37, 1.44	1.41	56.4	38.3	15.2	32.3, 33.1	53.1	32.7
39	43.1	43.1	1.55 (br. m)		1.49	1.37	56.8	41.3	17.4	33.0, 37.0	56.4	33.7
40	40.9	46.1	1.6 (br. m)		1.43	1.9	56.9	38.9	15.5	27.2, 33.5	53.3	33.3
41	40.6	49.4	1.6 (br. m)		1.49	1.43	53.3	28.2				
43	38.5	105[a]	1.63−1.89		1.48, 1.61	1.25	57.1	36.8	16.2	30.1, 32.1	50.6	32.2
44	37.9	150[b]	1.62 (m)	1.52 (t)	1.48, 1.61	1.25	55.0	37.0	16.9	30.7, 32.4	50.6	33.6
45	42.1	−	1.83 (m)	1.34 (t)	1.50, 1.71	1.28	57.5	36.4	14.7	31.3, 33.2	51.9	33.6
46	36.3	−	1.40−1.8 (m)		1.32, 1.24	1.15	54.8	36.9	17.0	30.5, 32.1	50.7	32.8
47	36.9	−	1.45−1.80 (m)		1.27, 1.37	1.19	54.6	36.9	18.0	31.3, 32.4	50.8	33.6
48	35.5	−	1.78 (m)	(br.)	1.64	1.26	54.0	36.4	17.8	33.0, 33.5	51.6	33.4
49	37.6	−	1.77 (m)	(br.)	1.62	1.30	56.4	36.5	17.6	32.1, 33.0	51.3	34.7

[a] Line width 780 Hz. [b] Line width 2600 Hz.

ploying diorganyldichorosilanes, trichloro(organyl)silanes or silicon tetrahalides.[8,22] The silanes must be sufficiently Lewis acidic. Thus, Me_3SiH and Ph_3SiH do not react with **1** in contrast to Me_2SiHCl and Ph_2SiH_2, although both are not strong Lewis acids but obviously of sufficient strength to induce the hydrosilylation of **1**. On the other hand, the hydrides Ph_3EH (E = Si, Ge) did not react with **1** in contrast to Me_3SnH, Bu_3SnH and Ph_3SnH. This indicates that steric factors also influence the hydrometallation of **1**. However, it was most surprising that with Ph_3SnH an umpolung of the insertion occurs. The imino nitrogen atom of **1** is protonated with formation of a B−Sn bond.

The organylmetal compounds LiR, MgR_2, ZnR_2, CdR_2, BR_3, AlR_3, GaR_3 and $InPh_3$ all react with **1** by organometallation. This is a new route to compounds of the type tmp−BR−N*t*Bu−ER_{n-1}. Paetzold et al. have studied the reactions of LiR compounds with the iminoboranes X−B=N−CMe_3 (X = Me, Et, Bu). These react in a 1:2 ratio and provided *N*-lithioazaborazoniaborate compounds.[34] However, with iminoboranes X−B≡N−CMe_3 [X = CMe_3, $N(SiMe_3)CMe_3$] *N*-lithioaminoboranes $LiN(CMe_3)$−BXR were obtained of which (TMEDA)$LiN(CMe_3)$−$B(CMe_3)_2$ was crystallographically characterised.[34] Usually, *N*-lithioaminoboranes are prepared by deprotonation of aminoboranes R_2B−NHR′, $RB(NHR')_2$ or $B(NHR)_3$.[35−40] Deprotonation of the diborylamine mes_2B−NH−$Bmes_2$ with LiR in diethyl ether leads to ionic $[(Et_2O)_3Li][N(Bmes_2)_2]$ with a linear BNB unit of an allenic type and short B−N bonds [1.343(5), 1.348(5) Å] due to the dicoordinate N atom,[36] while deprotonation of mes_2B−NH_2 gives dimeric $[(Et_2O)LiNHBmes_2]_2$.[37] In both cases the Li atoms are tricoordinate. In the latter case, the nitrogen atoms are tetracoordinate. Consequently, the B−N bond of the dimeric molecule is longer [1.386(4) Å] than in mes_2BNH_2. Association of *N*-lithioaminoboranes can be prevented by using multidentate bases as ligands as has been demonstrated for 9-*N*-lithio(trimethylstannylamino)borabicyclo-[3.3.1]nonane−pentamethylethylenetriamine.[39] The monomeric *N*-lithiodiaminoborane **32** is unique because in the solid state the intramolecular coordinative Li−N bond stabilises the tricoordination of the Li atom and the bulkiness of the groups at the two nitrogen atoms hinders association. The B2−N2 bond of **32** is at the shorter end for B−N bonds [1.361(4) Å] between tricoordinate B and N atoms indicating a high degree of π-bonding. However, the Li1−N1 bond is weak and is 0.2 Å longer than the Li1−N2 bond. This is a general observation for all the *N*-metallated diaminoboranes reported here (**19**, **32** and **35**) and many others of a similar type.[21] In solution, however, the coordinate Li1−N1 bond (also Mg−N, B−N, Al−N, Ga−N and In−N bonds) is opened as shown by only one ^1H or ^{13}C NMR signal for the methyl groups attached to the piperidino ring. For those where two or more signals were observed, one can assume that the ring structure with a coordinate N1−E bond is retained in solution as shown, for instance, for compounds **12**−**17**. In particular, the lithium compound **32** proved to be a versatile reagent and we will report on its chemistry in a forthcoming paper.[21]

Experimental Section

General: All experiments were performed under anhydrous conditions using Schlenk or vacuum-line techniques. Solvents were dried by conventional methods. Commercial chemicals were purified either by distillation, crystallisation or were used as supplied (solutions of LiR compounds). Several compounds were already available in our laboratory. The following compounds were prepared by literature methods: **1**,[4] $AlMe_3$−OEt_2,[40] Ph_3In−1,4-dioxane,[41] Ph_3Al,[42] thexylborane,[12] disiamylborane,[43,44] $HBCl_2$−SMe_2 and H_2BCl−SMe_2,[45] $HBBr_2$−SMe_2 and H_2BBr−SMe_2,[46] 9-BBN.[47] NMR: Bruker AC 200 (^7Li, ^{11}B, ^{119}Sn), Jeol GS270 (^1H, ^7Li, ^{11}B, ^{13}C, ^{14}N, ^{119}Sn), Jeol EX400 (^1H, ^{13}C) instruments. If not otherwise stated all NMR spectra were recorded in C_6D_6. References: $SiMe_4$ (int.), BF_3−OEt_2 (ext.), 1 M aqueous LiCl (ext.), C_6D_6 (int.), aqueous 1 M $NaNO_3$ (^{14}N), $SnMe_4$ (ext.). IR: Nicolet FT-IR spectrometer (liquids as capillary films, solids as nujol mulls). MS: Atlas CH7 instrument, 70 eV; reported data: mass, relative intensity, assignment. X-ray: Siemens P4 diffractometer equipped either with a scintillation counter or a CCD detector. Low-temperature device LT2, Mo-K_α radiation, graphite monochromator.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]-borane (2): A solution of H_3B−SMe_2 (0.39 mL, 7.0 M solution in hexane, 2.8 mmol) was added to a solution of **1** (2.9 mL of a 0.96 M solution, 2.8 mmol) in hexane. The reaction was slightly exothermic. After 24 h of stirring, all volatile components were removed at ambient temperature in vacuo. **2** remained as a colourless oil. ^1H (^{11}B-decoupled) NMR: δ = 3.91 (br., 2 H, BH_2), 4.77 (br., 1 H, BH) ppm. $C_{13}H_{30}B_2N_2$ (236.0): calcd. C 66.16, H 17.94, N 11.87; found C 64.76, H 17.25, N 11.67.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]diisopropylaminoborane (6): To a solution of freshly distilled diisopropylamine (0.42 mL, 3.0 mmol) in hexane (20 mL) was added at 0 °C a solution of BH_3−THF in hexane (1.0 M, 3.0 mL). After warming to ambient temperature, all volatile components were removed in vacuo leaving behind 0.44 g of H_3B−NH(*i*Pr)$_2$ {$\delta^{11}B$ = −20.58 [quat., $^1J(^1H^{11}B)$ = 96 Hz] ppm}. A solution of **1** in hexane (0.96 M, 3.10 mL, 3.0 mmol) was then added at −78 °C. No reaction occurred at room temperature. On heating to reflux overnight, the formation of **6** was noted by its ^{11}B NMR signal at δ = 50.6 ppm. The compound was isolated as a solid after removal of all volatile components in vacuo. Yield 0.82 g of **6** (98%). The ^1H NMR spectrum was not very informative as the signals were strongly overlapping.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]dicyclohexylborane (8): A solution of **1** (7.9 mL, 0.462 M, 3.6 mmol) in hexane was added with stirring to tetracyclohexyldiborane (0.65 g, 1.8 mmol). The diborane derivative dissolved slowly. About 2 h later, a precipitate formed. According to ^{11}B NMR spectroscopy the reaction was complete after 4 d. After removal of the solvent in vacuo, a colourless powder remained which proved to be pure **8**. Yield 1.4 g of **8** (98%), m.p. 122−124 °C. ^1H NMR: δ = 1.78 (br., 22 H, C_6H_{11}), 2.15 (br., 1 H, BH) ppm. ^{13}C NMR: δ = 24.1 (br., BC), 27.7 (*p*-C of C_6H_{11}), 28.7 (*m*-C), 28.9 (*o*-C) ppm. MS (70 eV): *m*/*z* (%) = 400 (75) [M^+], 385 (15) [M^+ − Me], 317 (100) [M^+ − C_6H_{11}] and others. $C_{25}H_{50}B_2N_2$ (400.31): calcd. C 75.01, H 12.59, N 7.00; found C 74.54, H 11.25, N 6.77.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]diisoamylborane (9): A solution of **1** (8.65 mL, 0.462 M, 4.0 mmol) in hexane was added with stirring to a hexane solution of freshly prepared

dimeric disiamylborane (4.0 mmol). ^{11}B NMR spectroscopic analysis showed that the hydroboration of **1** was complete after 24 h. Removal of volatile material in vacuo left an oily residue which turned out to be pure **9**. Yield 1.47 g (97%). ^{1}H NMR: δ = 3.78 (br., 1 H, BH), 1.36, 1.35 [each 3 H, B(CH*Me*)], 1.01, 1.08 (each 6 H, CH*Me*$_2$) ppm. ^{13}C NMR: δ = 16.6 (br., BC), 23.0 (CH*Me*$_2$), 22.7 (BCH*Me*), 55.7 (CH*Me*$_2$) ppm. MS (70 eV): *m*/*z* (%) = 376 (28) [M$^+$], 361 (14) [M$^+$ − Me], 319 (40) [M$^+$ − C$_4$H$_9$], 305 (100) [M$^+$ − C$_5$H$_{11}$], 235 (100) [305 − C$_5$H$_{10}$]$^+$, 222 (24) [235 − CH$_2$]$^+$ and fragments of lower mass. $C_{23}H_{50}B_2N_2$ (376.29): calcd. C 73.42, H 13.39, N 7.44; found C 74.25, H 13.66, N 7.80.

9-[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]-9-borabicyclo[3.3.1]nonane (10): A solution of dimeric 9-borabicyclo[3.3.1]nonane (0.30 g, 1.4 mmol) in pentane (30 mL) was cooled to −78 °C. A solution of **1** (12.3 mL, 0.277 M, 2.8 mmol) in pentane was then slowly added. After stirring for 2 h at ambient temperature, the reaction was complete. A light yellow oil remained after removal of the pentane in vacuo (50 Torr). After addition of hexane (1 mL) and cooling of the solution to −50 °C, a colourless powder of **10** precipitated. Yield 0.91 g (95%), m.p. 65−67 °C. ^{1}H NMR: δ = 1.05 (2 H, CH), 1.90 (br., 12 H, 6 CH$_2$) ppm. ^{13}C NMR: δ = 12.1 (br., BMe), 23.5 (C$_a$), 26.5 (C$_d$), 33.0 (C$_c$) 33.2 (C$_b$) ppm. ^{14}N NMR: δ = −231 ppm. MS (70 eV): *m*/*z* (%) = 344 (95) [M$^+$], 329 (90) [M$^+$ − Me], 288 (15) [M$^+$ − C$_4$H$_8$], 261 (93) [M$^+$ − C$_6$H$_9$], and fragments of lower mass. $C_{21}H_{42}B_2N_2$ (344.20): calcd. C 73.28, H 12.30, N 8.14; found C 75.43, H 12.75, N 7.83.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino](1,1,2-trimethylpropyl)borane (11): To freshly prepared *sym*-dithexyldiborane(6) (2.5 mmol) was added, with stirring, a solution of **1** (10.8 mL, 0.462 M, 5.0 mmol) in hexane. After stirring for 8 d. the reaction was complete as shown by ^{11}B NMR spectroscopy. After removal of the hexane in vacuo, a colourless, mobile liquid was left. Yield 1.19 g of **11** (98%). The compound decomposed on attempted distillation at 130 °C/10^{-2} Torr with formation of 2,3-dimethyl-2-butene (trapped at −196 °C and identified by NMR spectroscopy). ^{1}H NMR: δ = 0.91 [d, ^3J(^{1}H^{1}H) = 6.6 Hz, 6 H, CHMe$_2$], 0.94 (6 H, C*Me*$_2$) ppm. ^{13}C NMR: δ = 18.6 (CH$_2$), 22.5 (C*Me*$_2$), 29.0, (br., CB), 37.3 (*C*HMe$_2$) ppm. MS (70 eV): *m*/*z* (%) = 236 (32) [M$^+$ − C$_6$H$_{12}$], 180 (9) [236 − C$_4$H$_8$]$^+$, no M$^{\cdot+}$. $C_{19}H_{42}B_2N_2$ (320.18): calcd. C 71.28, H 13.23, N 8.75; found C 72.14, H 13.11, N 9.21.

{(*tert*-Butyl)[chloro(2,2,6,6-tetramethylpiperidino)boryl]amino}borane (14) and [(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]chloroborane (15): To an emulsion of BH$_2$Cl−SMe$_2$ in hexane (2.7 mmol in 1.60 mL) was added dropwise a hexane solution of **1** (10.3 mL, 0.267 M, 2.7 mmol). After stirring for 5 h, a clear solution resulted. All volatile materials were removed in vacuo leaving behind a colourless viscous oil. In C$_6$D$_6$, this solution showed the presence of two isomers. **14:** ^{11}B NMR: δ = −5.9 [t, ^1J(^{11}B^{1}H) = 125 Hz], 25.1 ppm (ratio 1:1). **15:** ^{11}B NMR: δ = 3.8 [d, ^1J(^{11}B^{1}H) = 125 Hz], 30.6 [d, ^1J(^{11}B^{1}H) = 142 Hz] ppm (ratio 1:1). In addition a signal for (tmpB−NCMe$_3$)$_2$ (δ^{11}B = 34.6 ppm) was observed. The mixture could not be separated by fractional distillation.

{[Bromo(2,2,6,6-tetramethylpiperidino)boryl](*tert*-butyl)amino}borane (16) and Bromo[(*tert*-butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]borane (17): In analogy to **15** the components H$_2$BBr−SMe$_2$ (1.50 mL, 1.5 M, 2.2 mmol) and **1** (4.87 mL, 0.462 M, 2.2 mmol) were allowed to react in hexane. After 24 h, neither of the two starting materials could be detected by ^{11}B NMR spectroscopy. Four new signals were present, both as pairs in a 1:1 ratio. **16:** ^{11}B NMR: δ = 2.4 [t, ^1J(^{11}B^{1}H) = 75 Hz], 30.8 (s) ppm. **17:** ^{11}B NMR: δ = 1.0 [d, ^1J(^{11}B^{1}H) = 50 Hz], 32.3 [d, ^1J(^{11}B^{1}H) = 105 Hz] ppm. The mixture of isomers was not characterised by elemental analysis.

{(*tert*-Butyl)[chloro(2,2,6,6-tetramethylpiperidino)boryl]amino}chloroborane (12): To a stirred solution of HBCl$_2$−SMe$_2$ (1.50 mL, 1.30 M, 1.9 mmol) was added dropwise a hexane solution of **1** (7.28 mL, 0.267 M, 1.9 mmol). After 48 h, the reaction was quantitative. Removal of the volatile material left behind a colourless oil. Yield 0.55 g of **12** (93%). IR: ṽ = 2480 (νBH), 1480, 1450 (νBN$_2$), 660 (νBCl) cm^{-1}. $C_{13}H_{28}B_2Cl_2N_2$ (304.9): calcd. C 51.21, H 9.26, N 9.89; found C 51.11, H 9.39, N 9.34.

Bromo{[bromo(2,2,6,6-tetramethylpiperidino)boryl](*tert*-butyl)amino}borane (13): In analogy to **12** a hexane solution of HBBr$_2$−SMe$_2$ (19 mL, 0.23 M, 4.4 mmol) was allowed to react with **1** (7.33 mL, 0.23 M, 4.4 mmol). The reaction was slightly exothermic. After heating for several minutes to reflux, all volatile materials were removed in vacuo. **13** was obtained as a colourless viscous oil. Yield 1.69 g of **13** (97%). $C_{13}H_{28}B_2Br_2N_2$ (313.89): calcd. C 49.70, H 8.92, N 8.92; found C 48.98, H 8.97, N 8.76.

Dimeric [(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]alane (19): A solution of **1** in hexane (18.7 mL, 0.186 M, 3.5 mmol) was diluted further with hexane (15 mL), cooled to −78 °C, and a solution of AlH$_3$−NMe$_3$ (0.31 g, 3.5 mmol in 25 mL of diethyl ether) was added dropwise with stirring. After warming the mixture to ambient temperature, the ^{11}B NMR spectrum showed a broad signal at δ = 34.7 ppm and doublet at δ = 27.1 ppm. The volume of the solution was then reduced by about 50%. After 1 d at −20 °C, crystals had separated. The majority of the crystals were well-developed prisms which proved to be **19**. The compound is very moisture-sensitive. Selected IR bands: ṽ = 2515, 2468 (ν$^{10/11}$BH), 1831 (νAlH), 1460 (νBN$_2$) cm^{-1}. $C_{25}H_{60}Al_2B_2N_4$ (504.37): calcd. C 61.92, H 11.99, N 11.11; found C 57.05, H 11.78, N 9.45.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]diisobutylalane (20): To a stirred solution of **1** (3.0 mL, 0.96 M, 2.9 mmol) in hexane was added a hexane solution of *i*Bu$_2$AlH (2.9 mL, 1.0 M diluted with 10 mL of hexane). After 24 h, the hexane was removed in vacuo leaving behind **20** as a colourless air- and moisture-sensitive liquid (1.05 g, 99%). ^{1}H NMR: δ = 0.46 [d, ^3J(^{1}H^{1}H) = 6.3 Hz, 4 H, AlC*H*$_2$], 1.22 [d, ^3J(^{1}H^{1}H) = 6.3 Hz, 12 H, CH(C*H*$_3$)$_2$], 2.20 [m, 2 H, C*H*(CH$_3$)$_2$] ppm. ^{13}C NMR: δ = 28.8, 29.2 [CH(*C*H$_3$)$_2$], 32.7 ppm; *C*H(CH$_3$)$_2$, Al*C* not observed. ^{27}Al NMR: δ = 109.5 ($h_{1/2}$ = 1960 Hz) ppm. IR: ṽ = 2460 cm^{-1} (νBH). $C_{21}H_{46}AlBN_2$ (364.41): calcd. C 69.22, H 12.72, N 7.69; found C 68.21, H 12.08, N 8.12.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]diphenylsilane (21): To a solution of Ph$_2$SiH$_2$ (0.415 g, 2.25 mmol) in toluene (10 mL) was added a solution of **1** (4.6 mL, 0.5 M) in hexane diluted with toluene (10 mL). The mixture was stirred for 2 weeks. After this time, the ^{11}B NMR signal of **1** could no longer be detected. Removal of the solvents left behind a colourless oil. Attempts at crystallisation were unsuccessful. Because the NMR spectroscopic data showed no impurities, no further purification attempts were deemed necessary. ^{1}H NMR: δ = 0.57 (SiMe$_2$), 7.10−9.0 (m, Ph) ppm. ^{13}C NMR: δ = 129.01, 129.53, 130.17, 136.17, 17.71 (Ph) ppm. ^{29}Si NMR: δ = −21.87 [^1J(^{1}H^{29}Si) = 21 Hz] ppm. Selected IR bands: ṽ = 2490, 2395 (νBH), 2120 (νSiH) cm^{-1}. $C_{25}H_{39}BN_2Si$ (406.2): calcd. C 73.96, H 9.68, N 6.89; found C 72.63, H 9.77, N 7.08.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinobory)amino]trichlorosilane (22): To a toluene solution of **1** (0.67 g, 3.0 mmol in 4.6 mL) was

added at 0 °C a solution of $SiHCl_3$ (0.4 mL, 0.54 g, 4.0 mmol) in toluene (6 mL). After stirring for 30 min, all volatile material was removed in vacuo. Distillation afforded 0.66 g of **22** (62%), b.p. 110−115 °C/0.005 Torr, m.p. 40 °C. ^{14}N NMR: δ = −235, −298 ppm. IR: $\tilde{\nu}$ = 2492, 2460 st (νBH) cm^{-1}. $C_{13}H_{28}BCl_3N_2Si$ (357.64): calcd. C 43.66, H 7.89, N 7.83; found C 43.06, H 8.04, N 7.93.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]chlorodimethylsilane (23): Me_2SiHCl (300 mg, 3.2 mmol) was cooled to −78 °C. A solution of **1** (0.71 g, 3.2 mmol) in toluene (4.9 mL) was then added. The solution was then allowed to warm to room temperature with stirring. All volatile materials were removed in vacuo and the remaining liquid distilled at 70 °C/10^{-3} Torr. Yield 0.96 g of **23** (95%), m.p. 25−26 °C. ^1H NMR: δ = 0.57 ($SiMe_2$), 5.3 (BH, at −54 °C) ppm. ^{13}C NMR: δ = 8.75 (SiC) ppm. ^{14}N NMR: δ = −248, −307 ppm. IR: $\tilde{\nu}$ = 2460 (sh), 2420 m (νBH) cm^{-1}. $C_{15}H_{34}BClN_2Si$ (316.80): calcd. C 56.87, H 10.82, N 8.84; found C 54.07, H 10.79, N 9.28. The same result was achieved in the presence of a small amount of hydroquinone as a catalyst.

[(*tert*-Butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]trimethylstannane (24): To a solution of **1** (0.44 g, 2.0 mmol) in hexane (14 mL) was added Me_3SnH (1 mL). After heating the mixture to 50 °C, the reaction was complete (^{11}B NMR). All volatile materials were removed in vacuo. The residue, a colourless oil, proved to be sufficiently pure. However, on distillation only **1** could be isolated, b.p. 100−130 °C/0.1 Torr. Yield (before distillation) 0.40 g of **24** (93%). ^1H NMR: δ = 0.4 [$^2J(^1H^{119}Sn)$ = 55.1 Hz), $SnMe_3$] ppm. ^{13}C NMR: δ = 2.11 [$^1J(^{13}C^{119}Sn)$ = 388 Hz, $SnMe_3$] ppm. IR: $\tilde{\nu}$ = 2413, 2385 m (νBH) cm^{-1}. $C_{16}H_{37}BN_2Sn$ (386.99): calcd. C 49.66, H 9.64, N 7.24; found C 49.43, H 9.31, N 7.21.

Tributyl[(*tert*-butyl)(2,2,6,6-tetramethylpiperidinoboryl)amino]stannane (25): A solution containing **1** (0.89 g, 4.0 mmol) and Bu_3SnH (1.32 mL, 5.0 mmol) in toluene (10 mL) was heated to 60 °C for 2 h. The ^{11}B NMR spectrum showed the absence of **1** and a new signal at δ = 39.6 ppm. Volatile materials were removed from the solution in vacuo (0.001 Torr). The remaining colourless oil was distilled. The fraction of b.p. 120−135 °C/0.001 Torr consisted of 90% **25** and 10% Bu_3SnH according to NMR spectroscopic data. ^1H NMR (only main component): δ = 0.8−1.5 (m, Bu) ppm. ^{13}C NMR: δ = 18.75 [$^1J(^{13}C^{119}Sn)$ = 360 Hz, C_α], 29.09 [$^2J(^{13}C^{119}Sn)$ = 16 Hz, C_β], 27.79 [$^3J(^{13}C^{119}Sn)$ = 76 Hz, C_γ], 13.79 (C_δ) ppm. IR: $\tilde{\nu}$ = 2415 sh, 2388 m (νBH) cm^{-1}.

(*tert*-Butyl)[(2,2,6,6-tetramethylpiperidino)(triphenylstannyl)boryl]amine (26): Ph_3SnH (0.53 g, 1.5 mmol) was dissolved in toluene (50 mL). A solution of **1** in hexane (5.6 mL, 0.27 M, 1.5 mmol) was then added with stirring. After stirring for 1 d, a single ^{11}B NMR resonance at δ = 44.6 ppm was observed. A solid residue was left after removing all volatile components in vacuo. The solid was crystallised from hexane (40 mL) at −80 °C. Yield 0.44 g of **26** (75%), m.p. 106 °C. ^1H NMR: δ = 7.19 (m, 9 H, *o*-Ph and *p*-Ph), 7.81(m, 6 H, *m*-Ph) ppm. ^{13}C NMR: δ = 128.1, 128., 138.2, 144.6 ppm. ^{119}Sn NMR signal not detectable. $C_{31}H_{43}BN_2Sn$ (573.17): calcd. C 64.90, H 7.50, N 4.98; found C 64.74, H 7.41, N 4.62.

Lithium (*tert*-Butyl)(2,2,6,6-tetramethylpiperidinophenylboryl)amide−Diethyl Ether (32): A hexane solution of **1** (0.89 M, 5.59 mL, 5.0 mmol) was cooled to −78 °C. A solution of PhLi in cyclohexane/diethyl ether (2.0 M, 2.8 mL, 5.0 mmol) was then added dropwise with stirring. After the clear solution had reached room temperature, a light yellow precipitate appeared which redissolved on continued stirring. The solution showed a ^{11}B NMR signal at δ = 33.3 ppm. The brownish solid that remained after evaporation of the solvents in vacuo was crystallised from toluene at −78 °C. Yield 1.55 g of **32** (61%), m.p. 162 °C. ^{13}C NMR: δ = 125.14, 126.44, 134.13 (Ph) ppm; BC not found. ^7Li NMR (hexane): δ = 2.3 ($h_{1/2}$ = 9.7 Hz) ppm. $C_{23}H_{42}BLiN_2O$ (380.34): calcd. C 72.63, H 11.13, N 7.37; found C 64.75, H 10.04, N 7.41.

Lithium (*tert*-Butyl)[methyl(2,2,6,6-tetramethylpiperidino)boryl]amide−Tetramethylethylenediamine (30-TMEDA): To a solution of **1** (13.6 mL, 0.22 M, 3.0 mmol) in hexane at −78 °C was added tetramethylethylenediamine (0.45 mL, 3.0 mmol). A solution of LiMe in diethyl ether was then added (1.88 mL, 1.6 M, diluted with 25 mL of diethyl ether). After the addition, the solution became a bluish colour but at room temperature the solution was colourless. Some solid had formed which was removed by filtration. Dissolved in C_6D_6, this solid proved to be tmp−BMe−$NCMe_3$Li. Two ^{11}B NMR signals were observed for the filtrate at δ = 35.3 (90%) and 39.6 ppm (10%). The signal at δ = 39.6 ppm increased in intensity with time.

(*tert*-Butyl)[methyl(2,2,6,6-tetramethylpiperidinoboryl)amino]catecholborane (31): A solution of **30−TMEDA** (3.0 mmol, 16 mL) was allowed to quickly reach room temperature. A solution of *B*-chlorocatecholborane (0.6 g, 3.0 mmol) in diethyl ether (15 mL) was then added with stirring. A white precipitated rapidly formed. The suspension was stirred for 3 h and the solid was then removed by filtration and the filtrate reduced in volume to about 20 mL in vacuo and kept at −20 °C. Crystals of **31** separated within 2 d. Yield 0.75 g (73%), m.p. 158 °C. ^1H NMR: δ = 0.78 (s, BMe), 6.69−1.76 (m, 5 H) ppm. ^{13}C NMR: δ = 110.0, 119.27, 150.55 (C_{arom}) ppm. $C_{20}H_{34}BN_2O_2$ (356.11): calcd. C 67.45, H 9.62, N 7.87; found C 67.42, H 9.51, N 7.83.

Reaction of 1 with Butyllithium: BuLi (7.46 mL of a 0.670 M hexane solution, 5 mmol) was stirred and cooled to −78 °C followed by addition of a hexane solution of **1** (3.2 mL, 1.57 M). After warming to room temperature, a yellow solution formed. Evaporation of the solvent in vacuo gave a yellow solid, m.p. 74−75 °C. It showed a ^{11}B NMR signal at δ = 33.6 ppm (about 70%) and two other signals in toluene solution. The ^1H and ^{13}C NMR spectra indicated that the product was not pure. Attempts at purification by sublimation or crystallisation were unsuccessful.

Reaction of 1 with *tert*-Butyllithium. Formation of 1,2,3,4-*tert*-Butyl-1,3,2,4-diazadiboretidine (28): To a stirred solution of **1** (7.46 mL, 0.670 M) in hexane at −78 °C was added a hexane solution of $LiCMe_3$ (3.13 mL, 1.60 M, 5 mmol). The mixture was then allowed to warm to room temperature with stirring to give a yellow solution. After removal of all volatile components in vacuo, a yellow solid remained which on sublimation at 40 °C/0.001 Torr yielded colourless crystals of the diazadiboretidine **28**, m.p. 58−60 °C. ^1H NMR: δ = 1.23 (s, $BCMe_3$), 1.32 ($NCMe_3$) ppm (ratio 1:1). ^{13}C NMR: δ = 30.5 ($BCMe_3$), 33.8 ($NCMe_3$), 49.5 ($NCMe_3$) ppm; BC not detected. ^{11}B NMR: δ = 41.1 ppm.

Butylmagnesium (*tert*-Butyl)[butyl(2,2,6,6-tetramethylpiperidino)boryl]amide (33): A hexane solution of **1** (17.5 mL, 0.114 M, 2.0 mmol) was further diluted with hexane (20 mL). To the stirred solution at −78 °C was added a hexane solution of $MgBu_2$ (2.0 mL, 1 M). At room temperature the solution showed only one ^{11}B NMR signal at δ = 37.5 ppm indicating a quantitative reaction. Removal of the volatile materials gave an oily, non-volatile, moisture-sensitive residue. Attempted crystallisation from pentane at low temperature afforded no crystals. Attempted distillation in vacuo led to decomposition. ^1H NMR: δ = 0.95, 1.04, 1.11, 1.91, 1.27, 1.38, 1.51, 1.59 (Bu groups) ppm. ^{13}C NMR: δ = 14.3, 19.2, 27.0,

27.8, 32.7, 38.6 (Bu) ppm. $C_{21}H_{45}BMgN_2$ (360.72): calcd. C 69.98, H 12.50, 7.76; found C 63.65, H 11.90, N 7.30.

Magnesium Bis{(*tert*-butyl)[butyl(2,2,6,6-tetramethylpiperidino)-boryl]amide} (34): Prepared in analogy to **33** from **1** (0.114 M solution, 22.0 mL, 2.4 mmol) and $MgBu_2$ (1.25 mL, 1 M, 1.25 mmol). Colourless oil, yield 0.7 g (95%). ^{11}B NMR: δ = 39.0 ppm. ^1H NMR: δ = 0.72−1.59 ppm (br. m, 2/4-H, 3-H, Bu). ^{13}C NMR: δ = 14.0, 27.5, 29.5, 31.8, 38.1 ppm (main signals). $C_{24}H_{72}B_2MgN_4$ (582.90): calcd. C 70.06, H 12.45, N 9.61; found C 67.61, H 12.02, N 8.74.

Methylzinc (*tert*-Butyl)[methyl(2,2,6,6-tetramethylpiperidino)boryl]-amide (35): To a stirred solution of **1** (0.27 M, 7.4 mL, 2.0 mmol), diluted with hexane (20 mL) at −78 °C, was added a solution of $ZnMe_2$ (0.09 M, 2.9 mL, 2.0 mmol), dissolved in toluene (10 mL). After the solution had attained ambient temperature, the volume of the solution was reduced to about 20 mL. At −78 °C, crystals appeared within a week. These were highly sensitive towards moisture. Recrystallisation at −40 °C from hexane yielded single crystals. The yield was not determined. ^1H NMR: δ = −0.09 (ZnMe), 0.62 (BMe) ppm. ^{13}C NMR: δ = −11.3 (ZnMe), 1.0 (br., BMe) ppm. $C_{15}H_{33}BN_2Zn$ (317.61): calcd. C 56.67, H 10.39, N 8.52; found C 52.44, H 9.75, N 8.49.

Zinc Bis{(*tert*-butyl)[methyl(2,2,6,6-tetramethylpiperidino)boryl]-amide} (36): Prepared in analogy to **35** from **1** (2.5 mmol) in hexane (40 mL) and $ZnMe_2$ (1.8 mL, 0.69 M, 1.25 mmol), dissolved in toluene (10 mL).**36** is a sticky oil from which no crystals could be obtained. Yield 0.64 g (96%). ^{11}B NMR: δ= 39.1 ppm. ^1H NMR: δ = 0.62 (BMe) ppm. ^{13}C NMR: δ = 1.32 (br., BMe) ppm. $C_{28}H_{60}B_2N_4Zn$ (539.81): calcd. C 62.40, H 11.13, N 10.04; found C 62.95, H 11.41, N 10.12.

Phenylcadmium (*tert*-Butyl)[phenyl(2,2,6,6-tetramethylpiperidino)-boryl]amide (37): A solution of **1** (3.2 mmol) in hexane (49 mL) was cooled to −78 °C. A solution of $CdPh_2$ (0.16 g, 3.2 mmol) in $CHCl_3$ (30 mL) was then added with stirring. At room temperature, all volatile materials were removed in vacuo and the oily residue treated with small quantities of toluene. From the resultant solution appeared some well-shaped crystals which proved to be $CdPh_2$. Concentration of the solution yielded **37** as a microcrystalline powder. Yield 1.19 g of **37** (76%), m.p. 160 °C (dec.). ^1H NMR: δ = 7.13, 7.21, 7.27, 7.53, 7.50, 7.71 (m, Ph) ppm. ^{13}C NMR: δ = 126.0, 126.8, 128.3, 132.9, 139.5 (Ph) ppm. $C_{25}H_{37}BCdN_2$ (488.36): calcd. C 61.43, H 7.63, N 5.73; found C 59.00, H 7.60, N 5.52.

{(*tert*-Butyl)[methyl(2,2,6,6-tetramethylpiperidino)boryl]amino}-dimethylborane (38): A solution of **1** in hexane (11.0 mL, 0.362 M,) was frozen at −196 °C and BMe_3 (4.1 mmol) condensed onto it. The mixture was allowed to slowly thaw. After 4 h of stirring, all volatile material was evaporated in vacuo at 50 Torr. A colourless oil remained. Yield 1.07 g of **38** (97%), m.p. 18−20 °C. ^1H NMR: δ = 0.58 (6 H, BMe_2), 0.82 (3 H, BMe) ppm. ^{13}C NMR: δ = 12.1 (br., BMe, BMe_2) ppm. ^{14}N NMR: δ = −230.6 ($h_{1/2}$ = 500 Hz) ppm. MS (70 eV): *m*/*z* (%) = 263 (1) [M^+ − Me], 222 (100) [$tmpBNCMe_3^+$]. $C_{16}H_{36}B_2N_2$ (278.10): calcd. C 69.10, H 13.05, N 10.07; found C 69.02, H 12.85, N 10.32.

{(*tert*-Butyl)[phenyl(2,2,6,6-tetramethylpiperidino)boryl]amino}-diphenylborane (39): To a suspension of BPh_3 (1.00 g, 4.1 mmol) in hexane (20 mL) was added a solution of **1** in hexane (14.7 mL, 0.283 M, 4.1 mmol). After stirring for 16 h, the ^{11}B NMR spectrum showed the absence of **1**. When the solvent was removed in vacuo a precipitate appeared which was isolated by filtration. A second crop was obtained from the filtrate. Yield 1.65 g of **39** (86%), m.p. 107−110 °C. ^1H NMR: δ = 7.25−8.04 ppm (m, 15 H, Ph). ^{13}C NMR: δ = 149.6 (br., BC), 125.9, 126.8, 127.4 130.8, 135.9, 138.8 (Ph), 149.6 (BC) ppm. MS (70 eV): *m*/*z* (%) = 464 (5) [M^+], 449 (15) [M^+ − Me], 387 (35) [M^+ − Ph], 299 (25) [M^+ − BPh_2], 222 (47) [**1**$^+$]. $C_{31}H_{42}B_2N_2$ (464.2): calcd. C 80.19, H 9.12, N 6.03; found C 78.02, H 9.05, N 5.80.

Dibutyl{(*tert*-butyl)[butyl(2,2,6,6-tetramethylpiperidino)boryl]-amino}borane (40): To a hexane solution of **1** (8.80 mL, 0.283 M, 2.5 mmol) at room temperature was added BBu_3 (0.40 g, 2.5 mmol) with a syringe. After stirring for 2 d, the reaction was complete. Volatile materials were then removed in vacuo. The remaining colourless oil of **40** solidified at −78 °C. Yield 0.95 g (94%). ^1H NMR: δ = 0.87−1.24 (several m, Bu) ppm. ^{13}C NMR: δ = 14.4 (Me of Bu), 20.1 (br., BC), 24.0 (br., N_2BC), 26.6, 27.0, 27., 30.2, 34.2 ($BCH_2CH_2CH_2Me$) ppm. $C_{25}H_{54}B_2N_2$ (404.34): calcd. C 74.26, H 13.46, N 6.93; found C 72.97, H 13.03, N 6.77.

9-{(*tert*-Butyl)[methyl(2,2,6,6-tetramethylpiperidino)boryl]-amino}-9-borabicyclo[3.3.1]nonane (41): A solution of **1** (2.5 mmol in 8.9 mL of hexane) at −78 °C was added to 9-methyl-9-borabicyclo[3.3.1]nonane (0.34 g, 2.5 mmol). Within 4 d, a clear solution had formed. Most of the solvent was then removed in vacuo and the solid material isolated by filtration. Yield 0.8 g of **41** (93%), m.p. 82 °C. The product was pure as shown by the NMR spectroscopic data. ^1H NMR: δ = 1.95 (br., 12 H) ppm. ^{13}C NMR: δ = 22.9 (C-α), 23.1 (C-β), 32.5 (C-γ) ppm.

{(*tert*-Butyl)[methyl(2,2,6,6-tetramethylpiperidino)boryl]amino}-dimethylalane (43): A hexane solution of $(AlMe_3)_2$ (0.95 mL, 2.19 M, 1.05 mmol) at −78 °C was added to a stirred solution of **1** in hexane (3.5 mL, 0.586 M, 2.1 mmol). At room temperature, the mixture was stirred for 24 h. The hexane was then removed. The remaining oil could not be distilled without decomposition. Yield 0.58 g of **43** (96%). Due to the high sensitivity of the oil towards moisture and air only an approximate elemental analysis was obtained, while the ^1H NMR spectrum showed the correct intensities for the CMe_3, $AlMe_2$ and BMe groups. The same compound was obtained by using $AlMe_3{\cdot}OEt_2$ instead of Al_2Me_6. Elemental analysis was performed without sufficient protection against the atmosphere. ^1H NMR: δ = −0.11 ($AlMe_2$), 0.78 (BMe) ppm. ^{13}C NMR: δ = 7.0 ($AlMe_2$), 18.9 (br., BMe) ppm. ^{27}Al NMR: δ = 105.9 ($h_{1/2}$ = 780 Hz) ppm. $C_{16}H_{30}AlBN_2$ (294.27): calcd. C 63.11, H 15.53, N 9.53; found C 51.82, H 9.04, N 7.93 (ratio C/H/N = 15:31:2).

{(*tert*-Butyl)[ethyl(2,2,6,6-tetramethylpiperidino)boryl]amino}-diethylalane (44): Prepared in analogy to **43**. $AlEt_3$ (0.38 g, 0.33 mmol) in hexane (3.3 mL), 10.9 mL of a hexane solution of **1** (0.306 mmol). Mobile, air- and moisture-sensitive liquid. Yield 1.11 g of **44** (98%). ^1H NMR: δ = 0.40 [q, $^3J(^1H^1H)$ = 7.3 Hz, 4 H, $AlCH_2$], 0.81−1.19 (m, 5 H, BEt), 1.42 [t, $^3J(^1H^1H)$ = 7.3 Hz, 6 H, $AlCH_2CH_3$] ppm. ^{13}C NMR: δ = 7.9 (br., $AlCH_2$), 10.7 ($AlCH_2CH_3$), 11.5 (BCH_2CH_3), 14.2 (br., BCH_2) ppm. MS (70 eV): *m*/*z* (%) = 336 (2) [M^+] and others. $C_{19}H_{42}AlBN_2$ (336.35): calcd. C 67.85, H 12.59, N 8.33; found C 62.97, H 11.84, N 7.69.

{(*tert*-Butyl)[phenyl(2,2,6,6-tetramethylpiperidino)boryl]amino}-diphenylalane (45): Obtained in analogy to **43**. To $AlPh_3$ (0.26 g, 1.0 mmol, 5 mL hexane) was added a solution of **1** in hexane (4.0 mL, 0.252 M, 1.0 mmol). The mixture was stirred for 4 d and the solid isolated by filtration (0.38 g). From the solution another crop of 0.08 g was obtained by partially removing the hexane. Yield: 0.46 g of **45** (95%), m.p. 168−170 °C (dec.). ^1H NMR ($CDCl_3$):δ = 7.22−8.11 (m, 15 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 126.8, 126.9, 127.1, 128.7, 134.1, 17.6, 139.2 (Ph) ppm.

$C_{31}H_{42}AlBN_2$ (480.49): calcd. C 77.49, H 8.81, N 5.83; found C 75.87, H 8.88, N 5.33.

{(*tert*-Butyl)[methyl(2,2,6,6-tetramethylpiperidino)boryl]amino}-dimethylgallane (46): At −78 °C a solution of **1** (10.9 mL, 0.306 M, 3.3 mmol) was slowly added to $GaMe_3$ (0.38 g, 3.3 mmol) with stirring. The mixture was stirred at ambient temperature for 5 d. Removal of the hexane left a colourless, highly air-sensitive mobile oil which proved to be pure **46** by NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ = −0.12 (6 H, $GaMe_2$), 0.58 (3 H, BMe) ppm. ^{13}C NMR ($CDCl_3$): δ= 3.3 (br., $GaMe_2$), 14.2 (br., BMe) ppm. IR: $\tilde{\nu}$ = 1370 ($\delta_{as}GaMe_2$), 1210 ($\delta_{sym}GaMe_2$) cm^{-1}. MS (70 eV): *m*/*z* (%) = 336 (1) [M$^+$], 321 (100) [M$^+$ − Me]. $C_{16}H_{36}BGaN_2$ (337.01): calcd. C 57.02, H 10.74, N 8.31; found C 61.52, H 10.96, N 7.87.

{(*tert*-Butyl)[ethyl(2,2,6,6-tetramethylpiperidino)boryl]amino}-diethylgallane (47): Obtained from $GaEt_3$ (0.34 g, 2.2 mmol) and **1** (7.2 mL, 0.306 M, 2.2 mmol); 24 h of stirring at ambient temperature. Colourless, mobile liquid, very moisture-sensitive. Due to the high sensitivity of the compound only an unsatisfactory C,H analysis was obtained. ^{13}C NMR ($CDCl_3$): δ = 10.8 (BCH_2CH_3), 11.4, 11.5 (GaEt), 14.0 (br., BCH_2CH_3) ppm. MS (70 eV, ^{11}B, ^{69}Ga): *m*/*z* (%) = 349 (7) [M$^+$ − Et], 239 (5) [tmpGaEt$^+$], 126 (100) [tmp$^+$ − Me]. $C_{19}H_{42}BGaN_2$ (379.09): calcd. C 60.20, H 11.17, N 7.39; found C 59.07, H 7.45, N 7.03.

{(*tert*-Butyl)[phenyl(2,2,6,6-tetramethylpiperidino)boryl]amino}-diphenylindane (48): Triphenylindium−1,4-dioxane (0.95 g, 2.2 mmol) in hexane (15 mL) was treated for 15 min with a hexane solution of **1** (7.2 mL, 0.306 M, 2.2 mmol). After 24 h of stirring, all volatile components were removed in vacuo and the solid **48** crystallised from a minimum amount of hexane. Yield 1.12 g (89%), m.p. 133−135 °C. ^{1}H NMR ($CDCl_3$): δ = 7.37−8.07 (m, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 126.5 (*p*-C), 126.9, 127.3 (*p*-, *m*-, *o*-C of BPh); 127.9, 134.0, 138.6 (*p*-, *m*-, *o*-Ph of $InPh_2$), 144.0 (br., *i*-C of BPh), 156.5 (br., *i*-C of $InPh_2$) ppm. MS (70 eV): *m*/*z* (%) = 568 (2) [M$^{\cdot+}$], 491 (5) [M$^+$ − Ph], and many others. $C_{31}H_{42}BInN_2$ (568.32): calcd. C 65.52, H 7.45, N 4.93; found C 53.37, H 7.30, N 4.93.

X-ray Structural Determinations: Single crystals were placed in perfluoro ether oil under a blanket of nitrogen in the case of very sensitive crystals at −40 °C and a suitable crystal was selected. It was mounted on the tip of a glass fibre which was placed on the goniometer head while cooling with a stream of nitrogen, generally held at −80 °C. After alignment, data were collected on five sets of 15 frames each, which were used to determine the unit cell (Program SMART).[48] Data collection was then started (in case of data collection with a CCD device, data on 1200 frames were collected). After data reduction (Program SAINT),[48] the cell parameters were determined with a larger set of data. No absorption correction was applied except in the case of compound **24**. All structures were solved by direct methods (SHELX97).[49] Non-hydrogen atoms were refined anisotropically. In most cases, the hydrogen atoms were placed in calculated positions using the riding-model approach. However, NH, BH and AlH hydrogen positions were taken from the difference Fourier maps and refined isotropically. Relevant data can be found in Table 7. CCDC-221516 to -221520 contain the supplementary crystallographic data for this paper. These data

Table 7. Crystallographic data and information regarding the data collection and structure solutions for compounds **19**, **26**, **31**, **32** and **35**

	19	**26**	**32**	**31**	**35**
Empirical formula	$C_{26}H_{59}N_4Al_2B_2$	$C_{31}H_{43}B_2BSn$	$C_{23}H_{42}N_2OBLi$	$C_{20}H_{34}N_2O_2B_2$	$C_{15}H_{33}N_2BZn$
Formula mass	503.35	573.17	380.34	356.11	317.61
Crystal size [mm]	0.1 × 0.2 × 0.25	0.20 × 0.30 × 0.30	0.21 × 0.10 × 0.30	0.5 × 0.5 × 0.6	0.15 × 0.15 × 0.1
Crystal system	triclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a [Å]	10.499(4)	9.6974(1)	9.772(8)	19.799(1)	9.5172(2)
b [Å]	11 016(4)	16.0246(1)	13.187(8)	11.4759(1)	17.1486(1)
c [Å]	14.822(8)	18.9810(2)	19.02(1)	9.044(1)	10.8449(1)
α [°]	89.82(2)	90	90	90	90
β [°]	71.75(2)	90	96.40(2)	90	91.459(1)
γ [°]	80.28(1)	90	90	90	90
V [Å]	1603(1)	2949.59(6)	2436(3)	2052.87(2)	1769.39(4)
Z	2	4	4	4	4
ρ (calcd.) [Mg/m^3]		1.291	1.037	1.152	1.192
μ [mm^{-1}]	0.111	0.0887	0.061	0.072	1.379
F(000)	558	1192	840	776	688
Index range	$-12 \le h \le 12$	$-12 \le h \le 12$	$-12 \le h \le 7$	$-22 \le h \le 22$	$-12 \le h \le 11$
	$-12 \le k \le 12$	$-20 \le k \le 20$	$-14 \le k \le 16$	$-13 \le k \le 13$	$-20 \le k \le 19$
	$-16 \le l \le 16$	$-22 \le l \le 24$	$-24 \le l \le 17$	$-9 \le l \le 10$	$-13 \le l \le 13$
2θ [°]	49.42	58.22	57.94	48.80	58.72
T [K]	183(2)	183(2)	183(2)	183(2)	183(2)
Reflections (collected)	7885	17229	6400	9728	10100
Reflections (unique)	4152	6204	4141	3181	3540
Reflections (observed) (4σ)	3482	5962	2646	2973	2969
R (int.)	0.0366	0.0201	0.0548	0.0370	0.0281
Variables	345	324	262	243	181
Weighting scheme *x*/*y*	0.0376/2.4969	0.0166/0.4828	0.0308/1.7488	0.0325/1.5867	0.03550/1.4932
GOOF	1.170	1.056	1.221	1.157	1.137
Final *R* (4σ)	0.0713	0.0193	0.0807	0.0615	0.0414
Final *wR*2	0.1497	0.0413	0.1422	0.1264	0.0879
Largest residual peak [e/Å^3]	0.492	0.220	0.166	0.234	0.466

can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

[1] P. Paetzold, *Adv. Inorg. Chem. Radiochem.* **1987**, *31*, 123−170.
[2] H. Nöth, *Angew. Chem.* **1988**, *100*, 1664−1684, *Angew. Chem. Int. Ed. Engl.* **1988**, *7*, 1603−1623.
[3] P. Paetzold, A. Richter, T. Thijssen, S. Würtemberg, *Chem. Ber.* **1979**, *112*, 3811−3827.
[4] H. Nöth, S. Weber, *Z. Naturforsch., Teil B* **1983**, *38*, 1460−1465.
[5] D. Männig, H. Nöth, M. Schwartz, S. Weber, U. Wietelmann, *Angew. Chem.* **1985**, *99*, 979−981, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 998−999.
[6] E. Bulak, T. Varnah, P. Paetzold, U. Englert, *Z. Allg. Anorg. Chem.* **1999**, *625*, 3−15.
[7] H. Braunschweig, I. Manners, P. Paetzold, *Z. Naturforsch., Teil B* **1990**, *5*, 1453−1454.
[8] U. Wietelmann, PhD Thesis, University of Munich, **1986**.
[9] J. Chandrasekharan, H. C. Brown, *J. Org. Chem.* **1985**, *50*, 5181−5187.
[10] H. C. Brown, J. Chandrasekharan, D. J. Nelson, *J. Am. Chem. Soc.* **1984**, *106*, 3768−3771.
[11] H. C. Brown, S. H. Gupta, *J. Organomet. Chem.* **1971**, *32*, C1−C3.
[12] H. C. Brown, G. J. Klender, *Inorg. Chem.* **1962**, *1*, 204−214.
[13] H. C. Brown, E. F. Knights, *J. Am. Chem. Soc.* **1968**, *90*, 5281−5283.
[14] H. C. Brown, J. J. Katz, E. Negishi, *J. Am. Chem. Soc.* **1972**, *94*, 4025−4027.
[15] E. Negishi, H. C. Brown, *Synthesis* **1972**, 196−197.
[16] H. C. Brown, E. Negishi, *J. Am. Chem. Soc.* **1967**, *89*, 5285−5287.
[17] Bond dissociation energies could be a reason for the 50:50 ratio for **15/17**: Δ_{diss} [kJ/mol]: B−H 380.4, B−Cl 443.0, B−Br 367.8; see W. L. Jolly, *Modern Inorganic Chemistry*, McGraw Hill, New York, **1984**.
[18] H. Nöth, S. Weber, *Chem. Ber.* **1985**, *118*, 2554−2556.
[19] H. Nöth, W. Rattay, U. Wietelmann, *Chem. Ber.* **1987**, *120*, 859−861.
[20] U. Braun, T. Habereder, H. Nöth. *Z. Naturforsch.*, manuscript accepted.
[21] U. Braun, T. Habereder, H. Nöth, *Eur. J. Inorg. Chem.*, manuscript submitted.
[22] B. Böck, PhD Thesis, University of Munich, **1989**.
[23] N. M. Yoon, Y. S. Gyoung, *J. Org. Chem.* **1985**, *50*, 2443−2450.
[24] H. Nöth, H. Suchy, *Z. Anorg. Allg. Chem.* **1966**, *344*, 44−66.
[25] H. Nöth, B. Wrackmeyer, "Nuclear Magnetic Resonance Spectroscopy of Boron Compounds", vol. 14 of *NMR, Basic Principles and Progress* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer Publishers, Berlin, Heidelberg, New York, **1978.**
[26] H. Nöth, S. Weber, *Z. Naturforsch., Teil B* **1983**, *38*, 1460−1464.
[27] M. Hesse, H. Meier, B. Zeeh, *Spektrokopische Methoden in der Organischen Chemie*, 3rd ed., Thieme Verlag, Stuttgart, New York, **1987**.
[28] T. Habereder, H. Nöth, *Eur. J. Inorg. Chem.* **2001**, 1665−1669.
[29] H. Strasdeit, I. Büsching, A.-K. Duhme, S. Pohl, *Acta Crystallogr., Sect. C* **1993**, *49*, 567−578.
[30] X-ray structural data of $C_{12}H_{10}Cd$ (266.60), colourless prism, monoclinic, space group $P2_1/n$, cell axes and angles: a = 5.6664(7), b = 8.8080(7), c = 10.492(1) Å, β = 96.163(2)°, V = 477.5(1) Å^3, Z = 2, μ = 2.230 mm^{-1}, d = 1.854 Mg/m^3, F(000) = 260, T = 193 K, Index ranges: $-6 \le h \le 6$, $-10 \le k \le 10$, $-12 \le l \le 12$, reflections (collected) 2682, reflections (independent) 940 (4σ), max./min. transmission 0.746/0.589, variables 61, data/parameter ratio = 15.4:1, $R1$ = 0.0285, $wR2$ = 0.0719, largest difference peak 0.439 e/Å^3. Bond lengths [Å] and bond angles [°]: Cd1−C1 2.124(3), C1−C2 1.381(5), C2−C3 1.400(5), C3−C4 1.377(5), C4- C5 1.382(5), C5−C6 1.387(5), C6−C1 1.401(6). C1−Cd1−C1A 180, C2−C1−C6 116.4(3), Cd1−C1−C2 123.2(3), Cd1−C1−C6 120.2(3).
[31] D. Grdenič, B. Kamenar, A. Nagl, *Acta Crystallogr., Sect. B* **1977**, *33*, 587−589.
[32] N. A. Bell, H. M. Shearer, C. D. Spencer, *Acta Crystallogr., Sect. C* **1983**, *39*, 1182−1185.
[33] G. D. Coates, D. Ridley, *J. Chem. Soc.* **1965**, 1870−1877.
[34] P. Paetzold, C. Pelzer, R. Boese, *Chem. Ber.* **1988**, *121*, 51−59.
[35] U. Braun, T. Habereder, H. Nöth, H. Piotrowsky, M. Warchhold, *Eur. J. Inorg. Chem.* **2001**, 1132−1145.
[36] H. Chen, R. A. Bartlett, M. M. Olmstead, P. P. Power, S. C. Shone, *J. Am. Chem. Soc.* **1990**, *112*, 1049−1055.
[37] R. A. Bartlett, H. Chen, H. V. Rasika Dias, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1988**, *110*, 446−449.
[38] H. Chen, R. A. Bartlett, M. M. Olmstead, P. P. Power, S. C. Shoner, *J. Am. Chem. Soc.* **1990**, *112*, 1048−1955.
[39] T. Seifert, W. Storch, M. Vosteen, *Eur. J. Inorg. Chem.* **1998**, 1343−1349.
[40] F. Schindler, H. Schmidbaur, G. Jonas, *Chem. Ber.* **1965**, *98*, 3345−3352.
[41] Houben-Weyl, *Methoden der Organischen Chemie*, Thieme Verlag, Stuttgart, **1978**, vol. 13/14.
[42] M. Martin, Diploma Thesis, University of Munich, **1956**.
[43] H. C. Brown, D. B. Bigley, S. K. Arora, N. M. Yoon, *J. Am. Chem. Soc.* **1970**, *92*, 7161−7167.
[44] H. C. Brown, A. K. Mandal, S. U. Kalkarni, *J. Org. Chem.* **1972**, *42*, 1392−1398.
[45] H. C. Brown, N. Ravindran, S. U. Kulkarni, *J. Org. Chem.* **1979**, *44*, 2417 −2421.
[46] H. C. Brown, N. Ravindran, *Inorg. Chem.* **1977**, *16*, 2938−2940.
[47] H. C. Brown, *Boranes in Organic Chemistry*, Cornell University Press, Ithaca, New York, **1972**.
[48] *SMART*, *SAINT*, Siemens Analytical Instruments, Madison, Version 4.1.
[49] G. W. Sheldrick, University of Göttingen, **1997**.

Received November 5, 2003
Early View Article
Published Online July 6, 2004

