ELSEVIER

Borole derivatives

XXI ☆, 2,5-Diphenyl-2,5-dihydro-1*H*-boroles; structures of *tert*-butyl-2,5-diphenyl-2,5-dihydro-1*H*-borole and of bis(tmeda)lithium 2,5-diphenyl-2,5-dihydro-1*H*-borolediide

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Abstract

The magnesium reagent $Mg(C_4H_4Ph_2)(THF)_3$ derived from (E,E)-1,4-diphenyl-1,3-butadiene reacts with boron dihalides $BCl_2(NR_2)$ (R = Me, Et, ^iPr) and $^tBuBF_2$ to give 2,5-dihydro-2,5-diphenyl-1*H*-boroles $2,5$-$Ph_2C_4H_4BNR_2$ (**1a–1c**) and $2,5$-$Ph_2C_4H_4B^tBu$ (**1d**) as mixtures of *cis–trans* isomers. *cis*-**1d** possesses a classical structure with a ring folding of 8° along the line C-2,C-5 of the C_4B ring. The dimethylamino compounds **1a** undergo metallation when treated with LDA in THF. After addition of TMEDA, the product can be crystallized from hexane–THF (2 : 1) as $[Li(TMEDA)]_2[2,5$-$Ph_2C_4H_2BNMe_2]$ (**3**). The structure of **3** is that of a contact ion triple with a triple-decker-like arrangement of the borole ring and two $[Li(TMEDA)]^+$ units.

Keywords: 2,5-Diphenyl-2,5-dihydro-1*H*-boroles; 2,5-dihydro-1*H*-borolediide; Borole dianion; Boron; Borole

1. Introduction

Syntheses of simple 2,5-dihydro-1*H*-boroles (3-borolenes) are known [2–4], including *C*-unsubstituted [2] and various *C*-alkyl derivatives [3,4]. Here we report some exploratory work on the 2,5-diphenyl derivatives **1a–1d** and the metallation of the 1-(dimethylamino) compound **1a** to give a new borole dianion 2^{2-}. The main aim of this paper is to communicate two structures: (i) that of the *tert*-butyl compound *cis*-**1d** which is the first structure of a *B*-alkyl-2,5-dihydro-1*H*-borole and (ii) that of $[Li(tmeda)]_2(2) \equiv 3$ which is the second structure with a borole dianion.

2. Results and discussion

2.1. Synthesis of 2,5-dihydro-2,5-diphenyl-1H-boroles

Simple 3-borolenes can readily be made from magnesium-butadiene and organoborondihalides [2,3]. We have applied this synthetic method to (E,E)-1,4-diphenyl-1,3-butadiene. This highly activated butadiene readily forms a magnesium adduct $Mg(C_4H_4Ph_2)$-$(THF)_3$ (**4**) which is well known [5] and has been characterized structurally [6]. Treatment with dichloro(dialkylamino)boranes $BCl_2(NR_2)$ (R = Me, Et, ^iPr) produces the corresponding 3-borolenes **1a–1c** in near quantitative yields (Scheme 1). The products **1a–1c** are obtained as yellowish oils which slowly solidify. Nuclear magnetic resonance (NMR) spectroscopic analysis (see below) shows that they are mixtures of *cis–trans* isomers. In the case of **1c** a single crystallization from hexane afforded crystals of the pure *cis* isomer (*cis*-**1c**).

☆ For part XX see Ref. [1]. Dedicated to Professor Henri Brunner on the occasion of his 60th birthday.

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1a-d

2²⁻
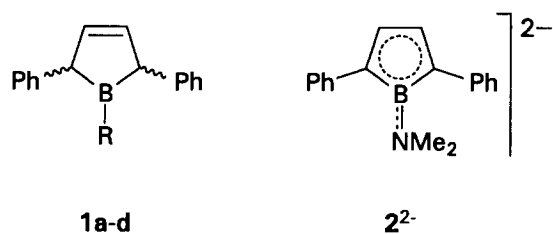
1a: R = NMe₂
1b: R = NEt₂
1c: R = N^{i}Pr₂
1d: R = ^{t}Bu

Two difficulties were encountered during the attempted synthesis of B-hydrocarbyl derivatives of type 1. One was ether cleavage of the THF which, for instance, was very fast in the reaction with MeBBr₂. The other difficulty appeared when Mg(C₄H₄Ph₂) (THF)₃ was treated with ^{t}BuBF₂. This reaction produced (E,E)-1,4-diphenyl-1,3-butadiene in mixture with cis-1d and trans-1d; fractionating crystallization afforded a small amount of pure cis-1d.

2.2. Distinction of cis and trans isomers 1a–1d

The new 2,5-dihydro-2,5-diphenyl-1H-boroles were essentially characterized by NMR spectroscopy. Both cis and trans isomers exhibit twofold symmetry in solution corresponding to C_s symmetry for the cis and C_2 symmetry for the trans isomers. However, the distinction of the two geometries was not straightforward. Both isomers display an AA'BB' spin system [7] for the four protons of the borole ring. This may be approximated as an AA'XX' spin system because of the relatively large shift difference (ca. 2.5 ppm) between the AA' and the BB' parts.

For 1a–1c, the XX' part (3-,4-H) displays an apparent triplet for the cis isomers and an apparent doublet for the trans isomers with small satellites in both cases. The AA' part (2-,5-H) is somewhat less well resolved. Keeping in mind that vicinal coupling constants always have positive signs [7] the spectra could be simulated with the coupling constants given in Fig. 1. For cis-1d the XX' part is seen as an apparent quartet with two

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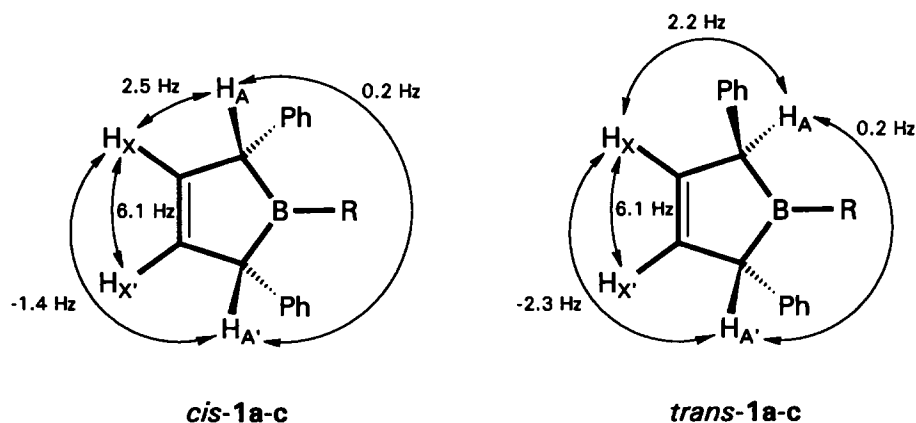cis-1a-c

trans-1a-c

Scheme 1.

cis-1a-c

trans-1a-c
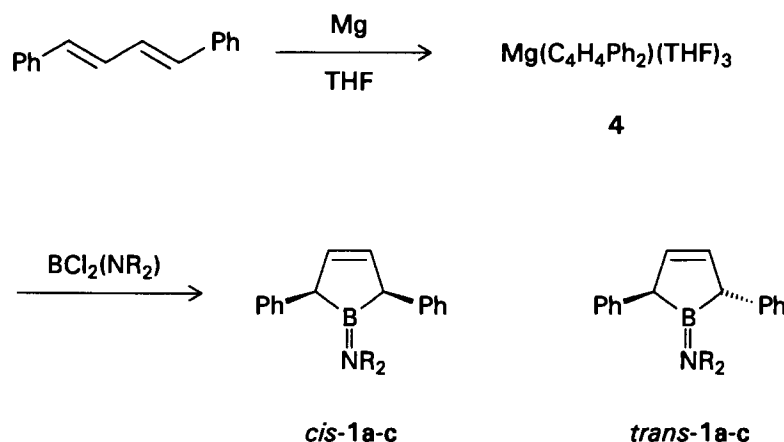
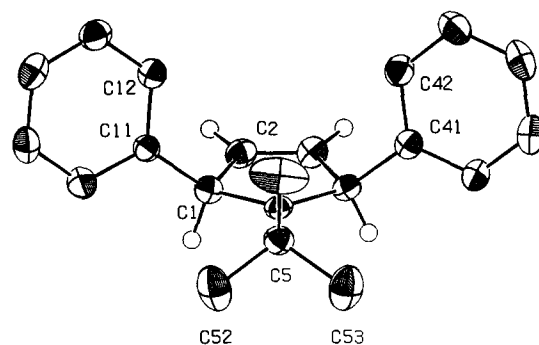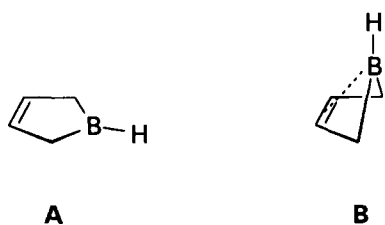Fig. 1. Coupling constants J_{HH} for the 2,5-dihydro-1H-boroles 1a–1c.

Fig. 2. The molecular structure of the 2,5-dihydro-1H-borole 1d with the crystallographic atom numbering scheme.

satellites, and simulation was possible with $J_{34} = 6.1$ Hz, $J_{23} = 2.5$ Hz, $J_{24} = -2.0$ Hz, and $J_{25} = 0$ Hz.

It seemed likely that the two Ph groups would increase the torsional angle 2-H,C-2,C-3,3-H if in cis disposition and hence would give rise to a smaller vicinal coupling constant J_{23} for the cis isomer. On this basis an assignment of the two isomers was feasible. However, a safer assignment was based on a comparison with 2,5-dihydro-1,1-dimethyl-2,5-diphenylsilole (5). Reaction of the magnesium reagent with Me$_2$SiCl$_2$ gave cis-5 as described in the literature [8] but with a small (7%) admixture of the trans isomer (Scheme 2). Here the assignment of the stereochemistry is unambiguous. While the dihydrosilole ring protons display the same AA'BB'-type spectra as in the case of the dihydroboroles 1, the two Si-methyl groups are chemically non-equivalent for cis-5 and symmetry related for trans-5.

2.3. Structure of the tert-butyl compound 1d

2,5-Dihydro-1H-boroles may have a classical structure A with a planar ring skeleton or alternatively a non-classical structure B with a folded ring skeleton and an interaction between the empty p$_z$ orbital of the boron and the π orbital of the olefinic double bond. For the parent compound C$_4$H$_4$BH, it has been shown by means of computational chemistry that the two structures are very close in energy, the difference being smaller than 1 kcal mol^{-1} [9].

Exocyclic substituents such as B-amino groups stabilize the classical structure A in agreement with the known structures of 1-amino-2,5-dihydro-1H-boroles which are indeed classical [10,11]. The non-classical structure B has been found in bicyclic systems where the bicyclic structure strongly favours the folding of the

dihydroborole ring [12]. The case of the phenyl derivative 3,4-Me$_2$C$_4$H$_4$BPh is interesting in that there is very little stabilization of the boron centre through π interaction with the phenyl substituent, yet this compound also displays the classical planar ring structure [4].

The tert-butyl group of compound 1d avoids π stabilization at the boron centre altogether. We also reasoned that the cis-2,5-diphenyl grouping would give rise to intramolecular repulsion between the two phenyl groups, and this repulsion would be avoided if the dihydroborole ring was folded. The structure determination (Fig. 2, Tables 1 and 2) reveals that this dihydroborole is nevertheless essentially planar. There is a small but significant folding of 8(1)° along the line C1,C4 of the dihydroborole ring. Thus the non-classical interaction with the olefinic double bond of the ring cannot be important.

2.4. Metallation of 2,5-Ph$_2$C$_4$H$_4$BNMe$_2$ (1a)

1-(Dimethylamino)-2,5-dihydro-1H-borole C$_4$H$_6$-BNMe$_2$ undergoes metallation when treated with suitable lithium dialkylamides and quaternization at boron when treated with alkyllithium reagents [13]. The stereoisomeric 2,5-diphenyl derivatives 1a react with LDA (LiN^{i}Pr$_2$) or LiTMP (lithium 2,2,6,6-tetramethylpiperidide) in THF to give a dilithio derivative which after addition of TMEDA (N,N,N',N'-tetramethylethylenediamine) can be crystallized as intensely yellow solid [Li(TMEDA)]$_2$[2,5-Ph$_2$C$_4$H$_2$BNMe$_2$] (3). Previously known compounds with borole dianions are
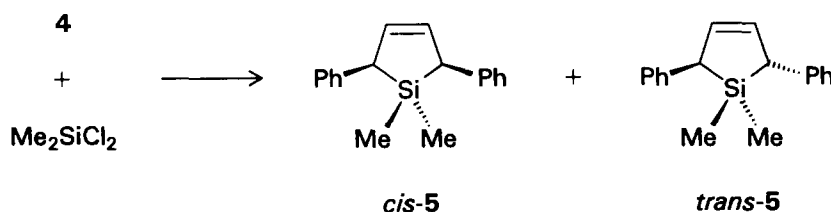
Scheme 2.

Table 1
Atomic coordinates of non-hydrogen atoms for **1d**

Atom	x	y	z	B_{eq} ($\times 10^4$ pm^2) [a]
C1	0.2197(5)	0.6282(2)	0.6641(1)	3.62(6)
C2	0.2878(5)	0.7122(2)	0.6977(2)	4.14(6)
C3	0.2856(4)	0.7133(2)	0.7719(2)	4.01(6)
C4	0.2177(5)	0.6301(2)	0.8075(1)	3.71(6)
C5	0.0489(5)	0.4823(2)	0.7379(2)	4.12(6)
C11	0.0517(5)	0.6337(2)	0.6002(1)	3.43(5)
C12	-0.1446(5)	0.6829(2)	0.6064(1)	4.01(6)
C13	-0.3000(5)	0.6871(2)	0.5488(2)	4.67(7)
C14	-0.2667(5)	0.6416(2)	0.4840(2)	4.85(7)
C15	-0.0747(6)	0.5932(2)	0.4761(1)	5.21(8)
C16	0.0865(6)	0.5903(2)	0.5333(2)	4.54(7)
C41	0.0516(5)	0.6394(2)	0.8719(1)	3.58(6)
C42	-0.1481(6)	0.6855(2)	0.8627(2)	4.39(7)
C43	-0.3022(6)	0.6958(2)	0.9210(2)	5.04(7)
C44	-0.2623(6)	0.6585(2)	0.9889(2)	5.44(8)
C45	-0.0647(6)	0.6111(2)	0.9992(2)	5.66(8)
C46	0.0888(5)	0.6028(2)	0.9416(2)	4.55(7)
C51	-0.2084(6)	0.4927(2)	0.7392(3)	8.9(1)
C52	0.1167(8)	0.4292(2)	0.6704(2)	7.2(1)
C53	0.1242(8)	0.4316(2)	0.8073(2)	7.0(1)
B	0.1504(5)	0.5734(2)	0.7370(2)	3.50(6)

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents, defined as $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}]$.

$K_2[C_4Ph_4BPh]$ [14,15], $Li_2[C_4H_4BN^iPr_2]$ [16], and $[Li_2(TMEDA)][C_4H_4BNR_2]$ (R = Me, Et, ^{i}Pr) [13].

The new compound **3** displays a boron resonance at $\delta(^{11}B) = 28$ ppm in the expected region. The ^{7}Li resonance is found at $\delta(^7Li) = -5.00$ ppm in THF (0.49 mol l^{-1}, ambient temperature). This chemical shift indicates facial bonding of the lithium to the C_4B ring system. For LiCp the corresponding resonance is found at $\delta(^7Li) = -8.37$ ppm (in THF, ambient temperature) [17] while the sandwich species $[LiCp_2]^-$ exhibits a resonance at $\delta(^7Li) = -13.1$ ppm (in THF, $-107°C$) [18]. The ^{13}C NMR data indicate considerable delocalization of the anion charge into the phenyl substituents.

Table 2
Selected bond distances (picometres) and bond angles (degrees) for **1d**

B–C1	161.0(4)	C4–B	158.9(4)
C1–C2	150.4(4)	C3–C4	150.9(4)
C2–C3	132.0(3)	B–C5	155.3(4)
C1–C11	150.7(4)	C4–C41	151.0(4)
C5–C51	151.7(4)	C5–C52	151.7(4)
C5–C53	153.4(4)		
C2–C1–C11	115.1(2)	C3–C4–C41	113.9(2)
C2–C1–B	102.5(2)	C3–C4–B	102.7(2)
C11–C1–B	118.3(2)	C41–C4–B	119.5(2)
C1–C2–C3	114.0(3)	C2–C3–C4	114.3(3)
C1–B–C5	126.8(3)	C4–B–C5	127.2(3)
C1–B–C4	105.9(2)		
C51–C5–B	106.3(2)	C51–C5–C52	109.4(3)
C52–C5–B	113.6(2)	C51–C5–C53	109.3(3)
C53–C5–B	112.2(2)	C52–C5–C53	106.1(2)

2.5. Structure of $[Li(TMEDA)]_2[2,5\text{-}Ph_2C_4H_2BNMe_2]$ (3)

The structure of **3** displays a triple-decker-like arrangement of the dianionic borole ring and two $[Li(TMEDA)]^+$ units (Fig. 3, Tables 3 and 4). The contact ion triple exhibits an approximate C_2 symmetry. The C_4BN moiety is essentially planar (maximum deviation 3.5(3) pm for C8). The various fragments of the anion deviate systematically from coplanarity to avoid strong repulsions between the N-methyl and the phenyl groups. Thus, the dimethylamino group is rotated by 25.9(3)° against the C_4B plane, and the two phenyl groups are rotated by 33.5(2)° and 33.9(2)° respectively.

There are indications that both the dimethylamino group and the phenyl groups perturb the aromatic dihydroborolediide ring. The B–N distance (147.0(4) pm) is between a typical double bond (141 pm [19]) and a representative B–N single bond (156 pm, between an NR_2 group and a trigonal boron atom as in $[Li(OEt_2)]_2[Ph(Me_2N)B=B(NMe_2)Ph]$ [20]). Furthermore, the C–B bonds in the ring (C6–B, 155.0(4) pm; C9–B, 154.1(4) pm) are significantly longer than in $[Li_2(TMEDA)][C_4H_4BNEt_2]$ (152.2(3) and 152.0(3) pm [13]). A comparison with calculated bond lengths (C–B, 155.9 pm; C=B, 139.0 pm) [21] also demonstrates the reduced contribution of C–B π bonding in **3**.

The $[Li(TMEDA)]^+$ units exhibit an asymmetric slip distortion, away from the boron and towards a trihapto bonding mode. This slip distortion clearly diminishes the non-bonding repulsions with the anion. It also implies an improved overlap with three ring carbon atoms and thus will increase covalent bonding contributions. This phenomenon is known as electrostatical orbital polarization [22,23].
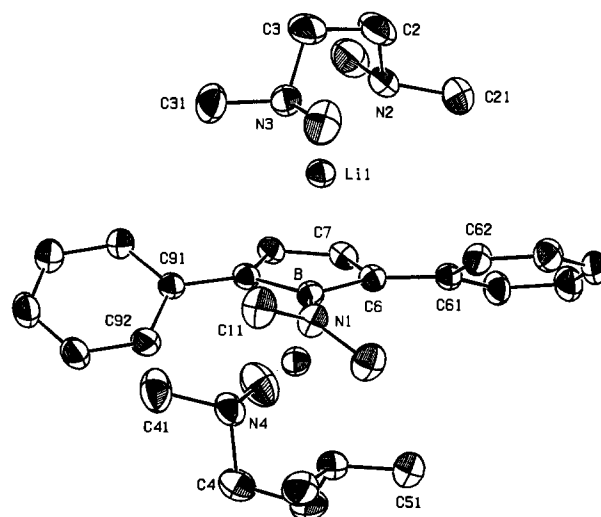

Fig. 3. The structure of the 2,5-dihydro-1H-borolediide **3** with the crystallographic atom numbering scheme.

3. Experimental details

Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Pentane and hexane were distilled from Na–K alloy and THF from sodium benzophenone ketyl. NMR spectra were recorded on Bruker WH 270 PFT (^{13}C, 67.9 MHz), JEOL NM-PS-100 (^{11}B, 32.08 MHz), Varian VXR 300 (^{1}H, 300 MHz, ^{13}C, 75.4 MHz), and Varian Unity 500 (^{1}H, 500 MHz; ^{6}Li, 73.6 MHz; ^{7}Li, 194.3 MHz; ^{13}C, 125.7 MHz) spectrometers. Mass spectra were recorded on a Varian MAT CH-5 spectrometer.

3.1. 1-(Dimethylamino)-2,5-dihydro-2,5-diphenyl-1H-borole (1a)

Magnesium–butadiene reagent **4** (5.8 g, 13.0 mmol) was suspended in hexane (or pentane) at −78°C and

Table 3
Atomic coordinates of non-hydrogen atoms for **3**

Atom	x	y	z	B_{eq} (×10^4 pm^2) [a]
N2	0.091	0.19744(6)	0.123	5.15(6)
N3	−0.2274(4)	0.16445(6)	−0.0377(3)	5.13(7)
C2	−0.0494(6)	0.21179(8)	−0.0098(4)	7.1(1)
C3	−0.1674(6)	0.18771(9)	−0.1161(4)	7.6(1)
C21	0.1667(6)	0.22103(9)	0.2447(4)	7.6(1)
C22	0.2254(5)	0.1855(1)	0.0839(5)	7.4(1)
C31	−0.2967(5)	0.13632(9)	−0.1314(4)	6.7(1)
C32	−0.3551(5)	0.1779(1)	0.0036(5)	7.5(1)
Li1	−0.0191(6)	0.1547(1)	0.1764(5)	4.1(1)
B	−0.1083(4)	0.12485(8)	0.3417(3)	3.44(6)
C6	0.0416(3)	0.14863(6)	0.4211(3)	3.33(5)
C7	0.1819(3)	0.13800(6)	0.3913(3)	3.54(5)
C8	0.1324(3)	0.11203(6)	0.2915(3)	3.50(5)
C9	−0.0380(3)	0.10135(6)	0.2624(3)	3.36(5)
N1	−0.2779(3)	0.12495(6)	0.3416(3)	4.32(5)
C11	−0.4313(4)	0.11153(9)	0.2216(4)	5.84(9)
C12	−0.3113(4)	0.13829(9)	0.4612(4)	5.82(8)
C61	0.0556(3)	0.17855(6)	0.5032(3)	3.62(6)
C62	−0.0872(4)	0.19849(7)	0.4662(3)	4.40(6)
C63	−0.0758(4)	0.22719(8)	0.5378(4)	5.34(8)
C64	0.0804(5)	0.23758(7)	0.6501(4)	5.81(9)
C65	0.2230(5)	0.21898(8)	0.6877(4)	5.65(9)
C66	0.2116(4)	0.18997(7)	0.6161(3)	4.66(7)
C91	−0.1054(3)	0.07167(6)	0.1807(3)	3.53(6)
C92	−0.2122(4)	0.05162(7)	0.2177(3)	4.48(7)
C93	−0.2731(4)	0.02298(7)	0.1453(4)	5.28(8)
C94	−0.2286(5)	0.01242(8)	0.0332(4)	5.87(9)
C95	−0.1234(5)	0.03100(8)	−0.0042(4)	5.65(9)
C96	−0.0630(4)	0.06014(7)	0.0672(3)	4.52(7)
Li2	0.1472(6)	0.0953(1)	0.5076(5)	4.0(1)
N4	0.3099(3)	0.05261(6)	0.5602(3)	5.08(6)
N5	0.1520(3)	0.08552(6)	0.7207(3)	5.12(6)
C4	0.2998(6)	0.03834(8)	0.6922(4)	7.2(1)
C5	0.2913(6)	0.06248(9)	0.7999(4)	7.7(1)
C41	0.2646(5)	0.02930(9)	0.4389(5)	7.4(1)
C42	0.4818(5)	0.06474(9)	0.5978(6)	7.6(1)
C51	0.1762(5)	0.11370(9)	0.8155(4)	6.7(1)
C52	−0.0179(5)	0.0726(1)	0.6796(4)	7.7(1)

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents, defined as $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos \beta)\beta_{13}]$.

Table 4
Selected bond distances (picometres) and bond angles (degrees) for **3**

B–C6	155.0(4)	B–C9	154.1(4)
C6–C7	144.3(4)	C8–C9	144.7(4)
C7–C8	140.2(4)	B–N1	147.0(4)
N1–C11	144.3(4)	N1–C12	143.9(4)
C6–C61	147.1(4)	C9–C91	146.0(3)
Li1–B	242.9(6)	Li2–B	243.1(5)
Li1–C6	222.6(5)	Li2–C6	243.5(5)
Li1–C7	216.9(5)	Li2–C7	222.2(6)
Li1–C8	221.6(5)	Li2–C8	217.8(6)
Li1–C9	243.0(5)	Li2–C9	223.3(5)
N2–C2	146.1(5)	N3–C3	147.4(5)
N2–C21	146.6(5)	N3–C31	145.6(4)
N2–C22	146.3(5)	N3–C32	145.1(5)
N2–Li1	221.1(6)	N3–Li1	211.4(5)
C2–C3	148.9(5)		
N4–C4	146.1(5)	N5–C5	147.4(5)
N4–C41	145.4(5)	N5–C51	146.4(5)
N4–C42	146.0(5)	N5–C52	144.9(5)
Li2–N4	220.1(5)	Li2–N5	210.7(6)
C4–C5	149.0(6)		
C7–C6–C61	120.2(2)	C8–C9–C91	120.0(2)
C7–C6–B	107.0(2)	C8–C9–B	107.3(2)
C61–C6–B	132.6(2)	C91–C9–B	132.4(2)
C6–C7–C8	111.0(2)	C7–C8–C9	110.6(2)
C6–B–N1	127.9(3)	C9–B–N1	128.3(3)
C6–B–C9	103.7(2)		
B–N1–C11	124.1(3)	B–N1–C12	124.2(2)
C11–N1–C12	111.7(2)		

BCl$_2$(NMe$_2$) [24] (1.64 g, 13.0 mmol) was added. Stirring was continued while the reaction mixture was allowed to warm up to ambient temperature. After the end of the reaction (ca. 3 h, as seen by ^{11}B NMR spectroscopy and by a change of colour) the MgCl$_2$ was filtered off and washed with several small portions of solvent. All volatiles were carefully removed from the filtrate in a vacuum. The residue was a yellowish oil which crystallized very slowly from hexane solution to give solid **1a** (3.23 g, 95%); air and water sensitive; cis : trans = 2.2 : 1 (NMR).

MS: m/e ($I_{rel.}$) = 261 (100, M), 170 (51, M − C$_7$H$_7$). ^{11}B NMR (CDCl$_3$): δ = 49.

cis-**1a**. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.15–7.35 (m, 2 Ph), 5.98 (m, 3-, 4-H), 3.27 (m, 2-, 5-H), 2.66 (s, NMe$_2$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ = 144.59 (C$_i$), 137.35 (C-3, 4), 129.05 and 128.34 (C$_o$ and C$_m$), 124.79 (C$_p$), 43.4 (C-2, 5), 40.93 (NMe$_2$).

trans-**1a**. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.15–7.35 (m, 2 Ph), 5.98 (m, 3-, 4-H), 3.38 (m, 2-, 5-H), 2.53 (s, NMe$_2$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ = 144.99 (C$_i$), 137.72 (C-3, 4), 128.64 and 128.15 (C$_o$ and C$_m$), 124.65 (C$_p$), 43.4 (C-2, 5), 40.53 (NMe$_2$).

3.2. 1-(Diethylamino)-2,5-dihydro-2,5-diphenyl-1H-borole (1b)

Treatment of **4** (5.8 g, 13.0 mmol) with BCl$_2$(NEt$_2$) [25] (1.82 g, 13.0 mmol) at 0°C, stirring at ambient temperature and workup as described for **1a** gave **1b**

(3.57 g, 95%); air and water sensitive; *cis*:*trans* = 1.1:1 (NMR).

MS: m/e $(I_{rel.})$ = 289 (75, M), 117 (94, $C_9H_8^+$). ^{11}B NMR (CDCl$_3$): δ = 49.

cis-**1b**. ^1H NMR (500 MHz, CDCl$_3$): δ = 7.15–7.35 (m, 2 Ph), 5.96 (m, 3-, 4-H), 3.26 (m, 2-, 5-H). NEt$_2$: 2.95 and 2.93 (dq, CH$_2$), 0.74 (t, 2 Me), $^2J_{11}$ = 14.0, $^3J_{12}$ = 7.0 Hz. $^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$): δ 145.05 (C$_i$), 137.33 (C-3,4), 128.85 and 128.35 (C$_o$ and C$_m$), 124.77 (C$_p$), 43.5 C-2,5), 43.27 (NCH$_2$), 14.47 (Me).

trans-**1a**. ^1H NMR (500 MHz, CDCl$_3$): δ = 7.15–7.35 (m, 2 Ph), 5.99 (m, 3-, 4-H), 3.37 (m, 2-, 5-H). NEt$_2$: 2.92 and 2.75 (dq, CH$_2$), 0.48 (t, 2 Me), $^2J_{11}$ = 14.0, $^3J_{12}$ = 7.0 Hz. $^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$): δ = 145.40 (C$_i$), 137.67 (C-3, 4), 128.49 and 128.28 (C$_o$ and C$_m$), 124.64 (C$_p$), 43.5 (C-2, 5), 42.71 (NCH$_2$), 13.94 (Me).

3.3.   1-(Diisopropylamino)-2,5-dihydro-2,5-diphenyl-1H-borole (1c)

Treatment of **4** (5.8 g, 13.0 mmol) with BCl$_2$ (N^{i}Pr$_2$) [26] (2.36 g, 13.0 mmol) at −78°C, stirring at ambient temperature (ca. 3 d) and workup as described for **1a** gave **1c** (3.9 g, 95%); air and water sensitive; *cis*:*trans* = 2.4:1 (NMR). A single crystallization from hexane gave 2.1 g (51%) of pure *cis*-**1c**.

MS: m/e $(I_{rel.})$ = 317 (70, M), 77 (100, Ph$^+$). ^{11}B NMR (CDCl$_3$): δ = 49.

cis-**1c**. ^1H NMR (500 MHz, CDCl$_3$): δ = 7.11–7.29 (m, 2 Ph), 5.89 (m, 3-, 4-H), 3.31 (m, 2-, 5-H). N^{i}Pr$_2$: 3.64 (sept, 2 CH), 0.98 and 0.90 (d, 2 Me), ^3J = 6.71 Hz. ^{13}C NMR (68 MHz, CDCl$_3$): δ = 145.01 (q, 7.3 Hz, C$_i$), 136.96 (dq, 160.4, 5.5 Hz, C-3, 4), 129.44 (dq, 156.1, 6.3 Hz, C$_o$), 128.30 (dd, 158.6, 7.0 Hz, C$_m$), 124.68 (dt, 160.2, 6.7 Hz, C$_p$), 44.35 (d, 115.8 Hz, C-2, 5). N^{i}Pr$_2$: 49.67 (d, 135 Hz, CH), 23.22 (qm, 125.5, 4.5 Hz, Me), 22.49 (qm, 125.4, 4.5 Hz, Me). The barrier to internal rotation about the C–N bond was determined by the coalescence method from ^{13}C spectra [27]: T_c = 243 K, $\Delta\nu$ = 612 Hz, $\Delta G^{\ddagger}$ = 44.2 kJ mol^{-1} for NCH; T_c = 223 K, $\Delta\nu$ = 89 Hz, $\Delta G^{\ddagger}$ = 43.9 kJ mol^{-1} for C$_i$; T_c = 223 K, $\Delta\nu$ = 101 Hz, $\Delta G^{\ddagger}$ = 43.7 kJ mol^{-1} for C-3, 4.

trans-**1c**. ^1H NMR (500 MHz, CDCl$_3$): δ = 7.11–7.29 (m, 2 Ph), 5.90 (m, 3-, 4-H), 3.41 (m, 2-, 5-H). N^{i}Pr$_2$: 3.45 (sept, 2 CH), 0.77 and 0.72 (d, 2 Me), ^3J = 6.71 Hz. $^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$): δ = 146.84 (C$_i$), 137.34 (C-3, 4), 129.00 (C$_o$), 128.25 (C$_m$), 124.65 (C$_p$), 44.3 (C-2, 5). N^{i}Pr$_2$: 49.6 (CH), 22.99 and 22.31 (Me).

3.4.   1-tert-Butyl-2,5-dihydro-2,5-diphenyl-1H-borole (1d)

The reaction of **4** with an equivalent of ^{t}BuBF$_2$ [28] at −78°C, workup as usual, gave a mixture of *cis*-**1d**,

trans-**1d**, and (E, E)-1,4-diphenyl-1,3-butadiene. Fractionating crystallization from hexane first removed the diene; further cooling to −30°C afforded colourless rod-shaped crystals of *cis*-**1d** (yield not determined); very air and water sensitive.

MS: m/e $(I_{rel.})$ = 247 (50, M), 142 (100, ?). ^{11}B NMR (CDCl$_3$): δ = 90 br.

cis-**1d**. ^1H NMR (500 MHz, CDCl$_3$): δ = 7.27 (m, 4 H$_o$), 7.13–7.18 (m, 4 H$_m$ + 2 H$_p$), 6.03 (m, 3-, 4-H), 3.48 (m, 2-, 5-H), 0.70 (s, ^{t}Bu). $^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$): δ = 142.74 (C$_i$), 136.85 (C-3, 4), 129.20 and 128.46 (C$_o$ and C$_m$), 125.28 (C$_p$), 51.2 (C-2, 5), 27.73 (Me), 27 (br, CMe$_3$).

trans-**1d**. ^1H NMR (300 MHz, CDCl$_3$): δ = 7.1–7.5 (m, 2 Ph), 6.07 (m, 3-, 4-H), 3.69 (m, 2-, 5-H), 0.87 (s, ^{t}Bu).

3.5.   2,5-Dihydro-1,1-dimethyl-2,5-diphenylsilole (5)

Treatment of **4** (4.1 g, 9.2 mmol) in pentane (80 ml) with Me$_2$SiCl$_2$ (1.1 ml, 9.0 mmol) at −78°C and workup as described for **1a** gave an oil. This was chromatographed on a short column of alumina and eluted until all material with a blue fluorescence (366 nm) had been passed through. Removal of the eluent left **5** (1.5 g, 63%) a colourless oil; *cis*:*trans* = 15:1 (NMR).

cis-**5**. NMR data as published [8].

trans-**5**. ^1H NMR (500 MHz, CDCl$_3$): δ = 6.18 (m, 3-, 4-H), 3.29 (m, 2-, 5-H), −0.18 (s, SiMe$_2$), remaining signals obscured by signals of *cis* isomer.

3.6.   Synthesis of [Li(TMEDA)]$_2$[2,5-Ph$_2$C$_4$H$_2$BNMe$_2$] (3)

1a (2.43 g, 9.3 mmol) in hexane (5 ml) was added dropwise with stirring to LiN^{i}Pr$_2$ [29] (19.0 mmol, prepared in situ from NH^{i}Pr$_2$ (2.7 ml) in THF (20 ml) and LiBu (11.9 ml, 1.6 m in hexane)). The colour of the mixture slowly turned red while it was allowed to warm up to ambient temperature. Stirring was continued for 24 h; monitoring the reaction by ^{11}B NMR spectroscopy is recommendable. After removal of the volatiles, the residue was washed with hexane, then dissolved with heating in a mixture of THF (20 ml), hexane (40 ml) and TMEDA (3 ml). Slow cooling to −78°C gave **3** (2.3 g, 49%) as large, vivid yellow crystals; air and water sensitive; darkens above 110°C; melting point ca. 150°C (dec.).

^1H NMR (500 MHz, THF-d_8): δ = 7.44 (d br, 7.6 Hz, 4 H$_o$), 6.92 (t br, 7.4 Hz, 4 H$_m$), 6.43 (t br, 7.1 Hz, 2 H$_p$), 5.87 (s, 3-, 4-H), 2.87 (s, NMe$_2$). TMEDA: 2.16 (s, 4 NCH$_2$), 1.98 (s, 8 NMe). $^{13}C\{^1H\}$ NMR (126 MHz, THF-d_8): δ = 149.32 (C$_i$), 127.53 and 125.14 (C$_o$ and C$_m$), 117.62 (C$_p$), 105.5 (br, C-2, 5), 100.07 (C-3, 4), 45.03 (NMe$_2$). TMEDA: 57.75 (NCH$_2$), 45.70 (NMe). ^7Li NMR (194.3 MHz, THF-d_8, 0.49 mol l^{-1}): δ = −5.00. ^{11}B NMR (THF-d_8): δ = 28.

Table 5
Crystallographic data, data collection parameters, and refinement parameters

Compound	1d	3
Formula	$C_{20}H_{23}B$	$C_{30}H_{50}BLi_2N_5$
Formula weight	274.22	505.46
Space group	$P2_12_12_1$ (no. 19)	Cc (no. 9)
a (pm)	586.1(2)	867.0(2)
b (pm)	1573.1(6)	4215.5(4)
c (pm)	1779.9(4)	978.4(1)
β (°)		116.288(9)
V (nm³)	1.642(2)	3.206(2)
Z	4	4
d(calc.) (g cm⁻³)	1.109	1.047
μ (cm⁻¹)	0.57	4.29
Temperature (°C)	−15	25
Radiation, λ (pm)	Mo K α, 71.07	Cu K α, 154.18
Crystal dimensions (mm³)	0.5×0.9×0.9	0.2×0.5×0.6
Measured reflections	2596	6455
Scan range	$3° \le \theta \le 25°$	$5° \le \theta \le 70°$
Scan type	ω	$\omega - 2\theta$
Absorption correction	None	None
Secondary extinction coefficient E	Not refined	1.46×10^{-5}
Observed independent reflections, $I > 1\sigma(I)$	1841	2678
Parameters refined	246	342
R [a], R_w [b]	0.055, 0.057	0.046, 0.054
Goodness of fit	1.430	1.233
Residual electron density (e pm⁻³)	0.3×10^{-6}	0.1×10^{-6}

[a] $R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w^{-1} = \sigma^2(F_o)$.

3.7. Structure determinations of 1d and 3

For both compounds geometry and intensity data were collected on ENRAF Nonius CAD4 diffractometers equipped with graphite monochromators. The structure solutions by direct methods (SHELXS-86 [30]) were straightforward and yielded the coordinates of all non-hydrogen atoms. The structures were refined with the SDP program package [31]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of 1d were refined isotropically except those at the tert-butyl group, which were treated as riding atoms with idealized geometry; all hydrogen atoms of 3 were also treated as riding atoms (C–H, 98 pm; $B(H) = 1.3B_{iso}(C)$). A statistical weighting scheme $w^{-1} = \sigma^2(F_o)$ was used for all reflections. Crystal data, data collection parameters, and convergence results are compiled in Table 5.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information m.b.H., D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-404122 (1d) and CSD-404121 (3).

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